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Fate of leaking natural gas in soil near oil and gas wells in Western Canada

by

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Abstract

Unwanted leakage of natural gas (>90 % v/v methane) occurs at ca. one third of the oil and gas wells in Western Canada. The $\delta^{13}C$ and concentrations of C_1-C_4 and CO_2 gases in soil gas samples collected from the heavy oil district of Alberta and Saskatchewan demonstrate that although aerobic bacterial oxidation of leaking gas in soil occurs at a number of well sites, there is little evidence for oxidation at many others. Long term monitoring at three leaking well sites demonstrated that methanotrophic bacteria metabolize >99 % v/v of the leaking gas in summer. Soil freezing, however, reduces oxidation by 60 % in winter. Oxidation of CH_4 is also inhibited in soil contaminated with heavy oil.

Estimated kinetic isotope fractionation factors $\varepsilon_{CH_4\text{-}CO_2}$ exhibit seasonal variability and correlate negatively with soil temperature. Results suggest that larger $\varepsilon_{CH_4\text{-}CO_2}$ values in winter are related to the lower activity of the Methane Mono Oxygenaze (MMO) enzyme at low temperature. Elevated soil H_2 contents and very low $\varepsilon_{CH_4\text{-}CO_2}$ values in the summer suggest that methanogenic microorganisms also inhabit the soils at well sites not contaminated with oil. The O_2 consuming methanotrophs provide habitats for the methanogens by rendering parts of the soil near the wells anaerobic. The low amount and comparatively high $\delta^{13}C$ of soil organic matter at those sites also suggest that fermentative bacteria from the methanogenic consortium metabolize biomass generated by the methanotrophs.

Authigenic calcites of bacteriogenic and abiotic origin, containing up to 100 % CH_4-derived carbon, precipitate in soils near the wells. The $\delta^{13}C$ and $\delta^{18}O$ of bacteriogenic calcite suggest that it forms in early spring, when soil temperature is too low for methanogenesis. This, along with the discovery of associated authigenic pyrite, suggests that the precipitation of bacteriogenic calcite may be related to the anaerobic oxidation of leaking gas.

This study should provide a strong impetus for the regulatory agencies in Western Canada to review their guidelines regarding leaking well remediation. Results also imply that a wider use of $\delta^{13}C$ analyses by the oil and gas industry may help to significantly reduce unwanted CH_4 emissions in Western Canada.

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to Galina, Monika, and Nikola

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Chapter 1

Introduction

Background and previous work

This dissertation is concerned with the microbial oxidation of natural gas in soils near leaking wells in Western Canada. More than three hundred thousand oil and gas wells have been drilled in the Western Canada Sedimentary Basin (WCSB) since the beginning of the last century. At least one third of those are impacted with unwanted leakage of natural gas along the well bore (Erno and Schmitz, 1996; Muehlenbachs, unpublished data). Conservative estimates, based on data from the references above, reveal that every year leaking wells in Western Canada contribute approximately 40000 tonnes of natural gas (predominantly methane) to the atmosphere. Although the atmospheric concentration of methane is only 175 ppb, on a molar basis methane traps twenty one times more heat than carbon dioxide (Whalen, 2005). The most important sink for atmospheric CH_4 is the troposphere where ca. 85 % of CH_4 is oxidized by hydroxyl (OH$^-$) molecules or broken down by UV light (Whalen, 2005). As a result, the half life of methane in the atmosphere is much shorter (i.e., 8-12 years) than that of carbon dioxide (i.e., ca. 200 years; Whalen, 2005). Therefore, targeted reduction of CH_4 of anthropogenic origin is expected to have a more rapid impact on radiative forcing than the reduction of CO_2 (IPCC, 2001).

Bacterial oxidation in soil is a sink for approximately 5 % of the atmospheric methane (Whalen, 2005). Incubation and field studies demonstrate that the principal factors that control aerobic bacterial oxidation of methane are the physical properties of soil (e.g., type and texture, porosity, and free air permeability), and climate factors such as moisture and temperature (Coleman *et al.*, 1981; Whalen *et al.* 1990; Happell *et al.*, 1993; Czepiel *et al.*, 1996; Borjesson and Svensson, 1997; Segers, 1998; Borjesson *et al.*, 2001). Soil air permeability controls the fluxes of both methane and oxygen and it is directly proportional to grain size and water saturation. The latter is also of particular importance to the rates of methane oxidation. Low soil water contents deprive bacteria of a medium to metabolize methane, whereas high water volumes reduce free air porosity and may starve the microorganisms by impeding gas diffusion (Czepiel *et al.*, 1996). Optimum water contents vary by soil type and depending on porosity are determined to be between 10 and 20 % v/v (Boeckx *et al.*, 1997, Christophersen *et al.*, 2000; Czepiel *et al.*, 1996; Whalen *et al.*, 1990).

Several studies demonstrate the detrimental impact of low soil temperatures on bacterial oxidation of methane (Whalen *et al.*, 1990; Borjesson and Svensson, 1997). Borjesson and Svensson (1997) argue that temperature alone accounts for 85 % of the observed variation in methane oxidation rates. Higher latitudes and strong continental climate in Western Canada result in air-temperature variability from +30°C in summer to -40°C in the winter. This variability renders soil temperature of particular importance to aerobic oxidation of leaking gas.

Aerobic methane oxidation comprises a set of reactions that result in the generation and consumption of three intermediate compounds (Hanson and Hanson, 1996):

$$CH_4 + O_2 \rightarrow CH_3OH \rightarrow HCHO \rightarrow HCOOH \rightarrow CO_2 \qquad [1\text{-}1]$$

Only a small fraction of methane carbon is converted to carbon dioxide, the rest being used for cellular growth and polysaccharide film production (cf. Borjesson *et al.*, 2001). Studies of natural gas seeps in both terrestrial and marine environments demonstrate that a portion of CO_2 produced from the oxidation of hydrocarbons is also trapped in the form of authigenic carbonate (Donovan *et al.*, 1974; Schumacher, 1996; Aloisi *et al.*, 2002). Authigenic soil carbonates form by combining soil carbon (HCO_3^-) and divalent metal ions (Ca^{2+}, Mg^{2+}, Fe^{2+}), the latter being the principal limiting factor to authigenic carbonate growth (Lal and Kimble, 2000). Precipitation of authigenic carbonates in soil is traditionally considered an inorganic process (Lal and Kimble, 2000), despite increasing evidence for the involvement of plants and microorganisms (Monger *et al.*, 1991; Cailleau *et al.*, 2005).

Microorganisms are associated with carbonate precipitation in marine, saline lake, soil and deep sediment environments (Boquet *et al.*, 1973; Hammes and Verstreate, 2002). Kidney stone formation and the precipitation of carbonate in the Martian meteorite ALH84001 are also attributed to microorganisms (Hammes and Verstreate, 2002). Some studies demonstrate the ability of microorganisms to precipitate and preserve carbonates even in environments where the physical characteristics of the medium are prohibitive of carbonate precipitation (Oelssner *et al.*, 2003).

Two major mechanisms of bacterially mediated carbonate precipitation are proposed by Castanier *et al.* (1999): active and passive. Active carbonatogenesis involves ionic transport of Ca^{2+} through the cell membranes of the microorganisms. During passive carbonate precipitation bacteria participate in the mineralization process by modifying the chemical composition of the local environment. Passive precipitation is a by-product of several metabolic pathways: the amino-acids ammonification; urea and uric acid degradation; and dissimilatory nitrate and sulphate reduction (Castanier *et al.*, 1999, McGenity and Selwood, 1999; Rivadeneyra *et al.*, 1998; Fujita *et al.*, 2000; Hammes *et al.*, 2003). Autotrophic metabolic pathways, such as non-methylotrophic methanogenesis and cyanobacterial photosynthesis, are also involved in carbonate precipitation, although heterotrophic carbonatogenesis is much more prevalent in marine environment (Castanier *et al.*, 1999). Bacteria and polysaccharide film provide nucleation sites and as a result carbonate minerals often precipitate on the cellular surfaces and in the microenvironments surrounding the cells (Merz-Preiss *et al.*, 1999; Warren *et al.*, 2001). Growth of calcite crystals within and on the top of microorganisms is considered the best evidence for active carbonate precipitation (Castanier *et al.*, 1999).

A variety of mineral textures are considered to reflect the involvement of microorganisms in carbonate precipitation. The most common ones are spheroid, rod, filamentous and vibrioid textures as well as ooid, fibrous, radial, and even dumbbell shapes (Monger *et al.*, 1991; Braissant *et al.*, 2003). Many irregular textures (including some listed above), however, have little to do with direct involvement of microorganisms, but have been attributed instead to supersaturation (e.g., crusts, radial aggregates) or the existence of micro gradients in the medium (e.g., dendritic textures; Hammes *et al.*, 2003, Henriksen *et al.*, 2002).

Estimated rates of inorganic authigenic carbonate precipitation in arid (uncontaminated) soils are slow (e.g., 1.10^{-6} to 1.10^{-5} $\text{mol.cm}^{-2}.\text{year}^{-1}$); Cerling, 1984). It is therefore assumed that carbonates precipitate in isotope equilibrium with ambient soil CO_2 and soil water (Cerling, 1984). Living systems, however, are known to significantly modify the stable isotope compositions of the byproducts of their metabolic activities (Hayes *et al.*, 1994). Thus, there is a possibility that bacteriogenically precipitated carbonate near the leaking wells may not be in isotope equilibrium with local soil CO_2 and soil water.

Authigenic carbonates near marine and terrestrial hydrocarbon seeps have $\delta^{13}C$ significantly lower than the $\delta^{13}C$ of calcite and dolomite of marine, fresh water or pedogenic origin (Donovan *et al.*, 1974; Aloisi *et al.*, 2002). The low $\delta^{13}C$ compositions of those carbonates indicate the incorporation of carbon produced during the oxidation of gaseous and/or liquid hydrocarbons. The precipitation of carbonates related to the microbial oxidation of methane at the seafloor is a common phenomenon, as carbonate reefs composed of methane-derived calcite are found in sediments as old as the Neoproterozoic (Jiang *et al.*, 2003). Authigenic sulphide minerals such as pyrite, greigite, pyrrhotyte, and maghemite are also common near hydrocarbon seeps (Schumacher, 1996; Aloisi *et al.*, 2002). The precipitation of sulphides is attributed to bacterial sulphate reduction (Schumacher, 1996). Sources of sulphur are H_2S gas or sulphur compounds in the oil and/or oil field water. The close spatial association of carbonates (calcite, Mg-calcite) with sulphide phases implies that carbonate precipitation is closely related to the anaerobic oxidation of gaseous or liquid hydrocarbons (Aloisi *et al.*, 2002).

The $\delta^{13}C$ and $\delta^{18}O$ compositions of authigenic soil carbonates provide a wealth of information ranging from conditions of precipitation to soil productivity (Cerling *et al.*, 1984). The principal factor that controls the isotope carbon composition of authigenic soil carbonates is the concentration and $\delta^{13}C$ of soil CO_2. The $\delta^{13}C$ of soil CO_2 depends on the $\delta^{13}C$ of soil organic matter (SOM), soil respiration rates and physical properties of the soil (air permeability, moisture, and temperature). The $\delta^{13}C$ of SOM is controlled by the proportion of C_3, C_4 and/or CAM plants that contribute, or have contributed in the past, organic matter to the soil (Cerling, 1984). Soil respiration is a combination of live plant root respiration and oxidation of soil organic matter by heterotrophic bacteria (Andrews *et al.*, 2000). In addition to the type and quantity of living plants and soil organic matter, soil respiration rates depend strongly on soil temperature and/or moisture (Boone *et al.*, 1998).

Objectives and overview

Leaking well sites are perfect laboratories where different microbiological processes related to the presence of gaseous and/or liquid hydrocarbon contamination can be studied in a natural setting. A common theme throughout this dissertation is the ability of stable isotopes to provide information about the nature and relative importance of these processes. The principal objective of this study is to determine the role bacterial oxidation plays in reducing the volume of leaking natural gas (methane) in the soil near the wells, and also to better understand the impact that environmental factors such as soil temperature, moisture, and the presence or absence of liquid hydrocarbon contamination may have on the ability of methanotrophic bacteria to metabolize leaking gas. Therefore, the first study of this dissertation (Chapter 3) focuses on the nature of the microbiological processes by investigating the relationship between the concentrations and carbon stable isotope compositions of hydrocarbon and (or) non-hydrocarbon soil gases and parameters such as soil temperature, pH, moisture, and soil water chemistry. The first part of Chapter 3 is concerned with the review of a large number of soil and surface casing vent (SCV) gas samples collected through the WCSB. The second part focuses on a large set of samples collected at different depths and distances from three leaking wells on a nearly monthly basis between 2001 and 2004. The amount of methane oxidized by aerobic methanotrophic bacteria in the soils at two of the research sites near the town of Edam, Saskatchewan is estimated by using the ratio of methane to carbon dioxide in the samples. Results presented here should be of particular interest to government regulatory agencies and the oil and gas industry in Canada.

The second objective of this dissertation is to determine what bacterially mediated Terminal Electron Acceptor Processes (TEAP), other than aerobic oxidation of hydrocarbons, may occur in soil near the leaking wells. Stable isotope compositions and concentrations of n-alkane and/or non-hydrocarbon gases such as CO_2 and H_2, and soil water chemistry are used to determine the type and/or estimate the relative significance of such processes.

The third objective of this dissertation is to study the type(s) and conditions of formation of authigenic mineral phases in soil near the leaking wells, with the hopes that results from this study may shed light on the nature of different TEAP's in the contaminated soils. Therefore, the second study of the dissertation (Chapter 4) focuses on the type, morphology, and origin (i.e., abiotic vs. bacteriogenic) of authigenic minerals (mostly calcite) in the soil at the monitoring well sites by using Scanning Electron Microscope (SEM) imaging and Energy Dispersive X-Ray (EDX) and X-ray Diffraction (XRD) techniques.

To better understand carbonate precipitation in uncontaminated soils near the leaking well sites, the third study (Chapter 5) determines the $\delta^{13}C$ composition of detrital and authigenic soil carbonate end-members near the two leaking wells at Edam. Measured are also the $\delta^{18}O$ compositions of soil moisture, $\delta^{13}C$ of soil CO_2 and soil organic matter as well as soil temperature. A one-dimensional diffusion model (Cerling, 1984) is used to estimate the soil respiration rates and, in conjunction with stable isotope measurements, to highlight the timing of authigenic carbonate precipitation.

The fourth study (Chapter 6) investigates the origin and the amount of authigenic soil carbonates near the leaking wells. Carbon and/or oxygen stable isotope compositions of soil carbonates, soil CO_2 and soil moisture are used along with soil moisture and temperature data for this purpose.

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Chapter 2

Study area and methodology

Study Area

Surface casing vent and soil gas samples from the University of Alberta database used in this study originate from a wide area in Alberta and Saskatchewan (i.e., Townships 19 through 68 and Ranges 21W4M to 18W3M, Figures 2-1 and 2-2). Most samples, however, were collected from well sites located around the town of Lloydminster located on the Alberta/Saskatchewan border. Three research sites equipped with permanent soil gas probes are located in Saskatchewan, two near the town of Edam and one near the town of Maidstone (Fig. 2-2).

Land in the area around Lloydminster is a transition between semiarid grassland to the south and boreal forest to the north, and it is mostly used for agriculture and oil production (cf. Van Stempvoort *et al.*, 1996). The surface topography comprises a gently rolling plain with an average elevation of 650 m. The climate in the area is semiarid with cold winters (Environment Canada, 2005). Mean annual air temperature varies from 4°C to the south to 1.4°C to the north (Landi, 2002). Air temperature differences between summer and winter are extreme reaching 60°C (Environment Canada, 2005).

Geology of the Lloydminster Area

A detailed description of the geology and stratigraphy of the Lloydminster area is outside the scope of this study. Reviews on the subject are available in the works of Orr *et al.* (1977), Virgas, (1977), Simpson (1984) and Jocksch *et al.* (1993), amongst others. Most resource wells drilled in the area produce heavy oil from the Lower Cretaceous Mannville Group, which comprises thick sand-shale cycles (Hayes *et al.*, 1994; Fig. 2-3). The contact between the Manville Group and the underlying carbonate rocks from the Devonian Duperow Formation is unconformable (White and

Schultz, 1977). The marine shales of the Cretaceous Colorado Group which cover the Mannville Group sediments (Lekie *et al.*, 1994) are the principal source of leaking gases in the area (Rich, 1995; Rowe, 1998). Those are covered with the Upper Cretaceous sediments of the Belly River Formation, from the uppermost Montana Group, which, on the other hand, are covered with glacial drift sediments of variable thickness (Van Stempvoort *et al.*, 1996, and the references therein). Depth to bedrock in the area varies from ca. 160 m (in the Maidsone area) to less than 50 m in the low lying areas and along the North Saskatchewan River valley (Van Stempvoort *et al.*, 1996; Fenton *et al.*, 2005). The most common lithology is gray till with laterally discontinuous sand and gravel horizons (cf. Van Stempvoort *et al.*, 1996).

Soil zones and types

A significant portion of the soils in Western Canada is developed on parent glacial tills (Landi, 2002). The distribution of the different soil types in Alberta and Saskatchewan coincides with the major ecoregions in the provinces. From south to north the soil zones are: Dry Brown; Dark Brown; Black; and Gray. The first two types correspond to the Prairie Grassland, the Black zone corresponds to the Aspen Parkland, and the Gray zone corresponds to the Boreal Forests (cf. Landi, 2002). The Edam and Maidstone research sites are located in the Gray and Black soil zones, respectively. Predominant soil type at Edam is the loamy sand to fine sandy loam, whereas loam to silty loam is the dominant soil type at Maidstone (Saskatchewan Watershed Authority, 2005).

A total of twenty-four well sites in the Lloydminster area were screened during this study for permanent soil gas monitoring sites in the summer of 2001. Soil compositions at those sites vary from gravel and sand, of apparent extraneous origin, to medium dark-brown clayey loam. Drilling for oil and gas has been associated with significant disturbance and contamination of the soil at the well sites. Often soils are contaminated with diesel fuel, drilling mud and various chemicals, and, in many instances, produced heavy oil and/or brine. Most leases in areas, where soil has high clay content, are often covered with gravel or sand (Fig. 2-4). In addition, excavations at the wellheads are often backfilled with transported soil and sediment or cement. At many sites, soil around the wells is repeatedly disturbed by the placement (and replacement) of oil and gas pipelines, and communication and power lines. At a number of leaking well sites soil is excavated to depths between 2.0 to 3.5 m and the wells are equipped with improvised leaking gas capturing devices. Those devices consist of LDPE "hoods" secured to the well casing with PVC tape and connected to the surface through a PVC tubing open to the atmosphere. As a result of the disturbance discussed above, the term "soil" used in this study has a descriptive rather than a genetic meaning.

The presence of heavy oil contamination at the leaking well sites was of particular concern to the outcome of this study. Thus, to examine its impact on the oxidation of leaking natural gas, permanent soil gas probes were installed at both "clean" and contaminated well sites. The two "clean" monitoring sites are located to the southeast of the town of Edam, Saskatchewan (i.e., A3 and A4-17-048-19W3[1]), whereas the contaminated site is located to the north of the town of Maidstone, Saskatchewan (i.e., A10-11-048-23W3).

Edam research sites

The two well sites are at a distance of approximately 400 m from each other. The high sand content renders soil in the area unfit for tillage (Fig. 2.6). Production records indicate that wells A3 and A4 were drilled in October 1997, but never produced oil and were suspended shortly after (IHS Energy, 2001). Therefore, it was assumed that soil at the two sites is not contaminated with heavy oil. Shallow exploratory drilling prior to and during the installation of the soil gas probes confirmed that soils at the sites are clean of visible liquid hydrocarbon contamination.

There is little or no vegetation near well A3 (Fig. 2.6), whereas tall grass and low shrub vegetation grows near well A4 (Fig. 2-7). It is also worth noting that there is a significant difference in the micro relief at the two sites. Soil surface at well A3 is flat, whereas well A4 is located in a small depression that is about 0.8 m deep and has a diameter of about 2.0 metres. Drilling of one exploratory well to a depth of 6.0 m, followed by drilling of a number of shallow holes for the soil gas probes, revealed that the Edam area is covered by a horizon of variable thickness (1.3 to 3.5 m) that consists of medium-grained sand. The uppermost soil horizon (e.g., <0.2 mbs) near well A4 (outside the small depression) consists of a silt-size dark-gray layer of apparent aeolian origin. The presence of sub-horizontal calcareous layers and concretions in the black topsoil collected at 1.0 and 2.0 m away from well A4, suggests that this horizon is a natural part of the soil profile in this part of the area.

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[1] An abridged version that includes only the first characters of the well LSD will be used for the three monitoring well sites throughout the thesis.

The sand horizon is underlain by clay-rich sediment with unknown thickness. The sand/clay contact at well A3 is located at 2.8 mbs. Depth from surface to the sand/clay contact at A4 is between 1.5 m in the depression near the wellhead and 2.1 m from 1.0 to 4.0 m away from the wellhead. Depth to the groundwater table was determined on four occasions during a three-year monitoring period. The average depth to the water table at wells A3 and A4 (outside the depression) is 2.3 and 2.0 m, respectively.

Maidstone research site

The lease around well A10 is covered by a gravel layer with an average thickness of 0.1-0.5 m. Coarse to medium sand with small amounts of gravel and clay underlies the gravel. Green-gray clayey loam starts between 0.8 and 1.1 mbs. Several metres away from the wellhead the gravel cover thins out and local soil crops out. Soil outside the lease is brown-grey silty to clayey loam. Agricultural activities start approximately 15 m away from well. Depth to the saturated zone could not be determined at this site. One soil gas probe screened at 1.65 mbs (metres below surface) and one of the probes screened at 1.0 mbs yielded water almost every time, indicating that that the clayey loam has high water retention and low permeability.

Shallow drilling revealed a large (ca. 25 m^2) subsurface oil spill at the lease. Heavy oil saturates completely the sandy horizon to the west of the well where the spill reaches 1.0 mbs and the thickness of the contaminated sand averages 0.3 m. Production records indicate that well A10 was drilled in 1964 and was suspended shortly after (IHS Energy, 2001). The lack of contamination at the surface suggests that the upper soil was excavated after the spill. The excavation was apparently backfilled with sand and covered with gravel.

Aberfeldy well sites

The Aberfeldy oil field is located approximately 5 km to the east of Lloydminster. Although no long term monitoring of soil gas compositions was done at Aberfeldy, Husky Energy and GChem Ltd. provided the rare opportunity to collect soil and carbonate scale samples from excavations at six leaking well sites. The wells are located on sections 16-, 17- and 20- of 049-26W3, and soil around the wells was excavated in the fall of 2003. None of the wells had surface casings. Soil in the area is gray to dark gray-brown silty to clayey loam. Average depth to the water table is estimated at 2.5 m.

Sample collection, selection, preparation and analysis

Soil gas sample collection

Permanent soil gas probes installed at the three monitoring sites consist of galvanized steel pipes with an internal diameter of 12.5 mm. A short screen at the bottom of each probe is connected to a brass valve fitted with a septum through HDPE tubing. Permanent probes were installed in vertical holes with an internal diameter of five or seven centimetres. The holes were drilled either with a hand auger, or with a mobile drilling unit provided by GChem Ltd. The bottom 0.2 m of the hole was filled with coarse quartz sand. The rest of the hole was packed with bentonite pellets. To collect shallow soil gas samples at the three sites, bottomless 4000 cm^3 glass containers with screw tops were installed at depths between 0.2 and 0.3 m. Probe locations are given in Table 2-1.

Soil gas sampling was conducted at relatively regular time intervals. Approximately two to three times the estimated volume of the LDPE tubing was purged prior to soil gas collection. Gas samples from the bottomless glass containers were collected with a screwed air-tight plastic lid fitted with a Swagelok™ fitting and a septum. About 300 cm^3 of soil gas were purged prior to sample collection. All soil gas samples were collected with a 150 ml HDPE syringe and transferred to pre-evacuated 120 ml serum glass bottles. The bottles were cleaned with 99.9 % n-propyl alcohol and distilled water and baked at 200°C for 8 hours at the GChem Ltd. laboratory. The bottles were then sealed with n-butyl stoppers (Belco Glass Inc.) and open centre alumina crimp caps.

Soil sample collection

In addition to the soil gas monitoring sites near Edam, Maidstone, and the six wells at Aberfeldy, Saskatchewan, soil samples for soil carbonate, pH, soil organic matter, and soil moisture measurements were collected at fifteen other well sites. Samples at the monitoring sites were collected at the same locations where the permanent soil gas probes were installed. At the rest of the well sites soil samples were collected as close as possible to the well casing at depths between 0.7 and 1.0 mbs.

Immediately after collection soil samples were sealed in glass containers with screwed caps (100 and 250 ml) and stored on ice. Upon arrival at University of Aberta the samples were placed in a freezer.

Soil gas compositions

Concentrations of light hydrocarbon gases (i.e., CH_4, to C_5H_{10}) in soil gas samples were determined in the G-Chem Ltd. laboratory, Lloydminster, on two Series II Hewlett Packard 5890 gas chromatographs equipped with a GC Alumina 30 m x 0.53 mm ID column (Scientific Instrument Services, Inc.) and a FID detector, using He as carrier gas. Concentrations of H_2, He, and O_2 were determined using a Molsieve 5A column (Varian Inc.), using Ar as carrier gas. ChemStation A.06.03 software by Agilent Technologies was used to integrate the data. Reproducibility for all species is better than ±5 %. The lower detection limit of light hydrocarbon gases is 5 ppb. Carbon dioxide concentrations were determined on a Gas Chromatograph combustion Continuous Flow Isotope Ratio Mass Spectrometer (GC-CF-IRMS) system at the University of Alberta. The lower detection limit for CO_2 concentration measurements is 100 ppm.

Carbon stable isotope analysis of hydrocarbon gases and CO_2

The carbon stable isotope analysis of light hydrocarbon gases and CO_2 were performed on a GC-C CF-IRMS at the University of Alberta. The gas chromatograph module consists of a Hewlett Packard 5890 gas chromatograph equipped with a Poraplot Q column. The GC is connected to a Finnigan 252 Isotope Ratio Mass Spectrometer. More information on the GC-C CF-IRMS set up is available in Rowe (1998). The working reference gas (CO_2) of the GC-C CF-IRMS system was calibrated to the VPDB scale using the NBS-18 and NBS-19 standards. Results are reported in the standard delta notation with respect to the VPDB and VSMOW standards (i.e., Coplen, 1995), respectively:

$$\delta^{13}C = \left(\left(\frac{R_{sample}}{R_{standard}} \right) - 1 \right) \times 1000 \quad [2\text{-}1]$$

where R_{sample} is the $^{13}C/^{12}C$ ratio of the sample and $R_{standard}$ is the $^{13}C/^{12}C$ ratio of a reference standard. Analyses of the International Atomic Energy Agency (IAEA) reference gas NGC-3 produced an average value of -72.38 ± 0.07 ‰ (n = 7). Reproducibility for the $\delta^{13}C$ analyses of C_1-C_5 and CO_2 is given in Table 2-3.

Sample selection, Scanning Electron Microscopy (SEM) imaging and Energy Dispersive X-ray (EDX) analysis

Aggregates of mineral grains cemented by authigenic calcite were selected for optical and SEM studies from samples collected in soil near the three monitoring sites. In addition, fragments of calcite crusts from the casings of well C4 at Aberfeldy were also handpicked for a SEM study. Soil samples were examined under a binocular microscope. Samples selected for SEM imaging were placed in glass vials and frozen to prevent sample deterioration. Prior to SEM imaging samples were sputter-coated with iridium. Iridium was chosen because it provides an exceptionally thin (ca. 40 A°) and stable conductive film that allows delicate structures to be resolved (Banerjee and Muehlenbachs, 2003). Scanning electron microscopy (SEM) observations were performed on a JEOL JSM-6301FXV electron microscope connected to a Princeton Gamma Tech IMIX energy-dispersive spectrometer system with a converted Noran detector. Semi quantitative analyses of mineral grains were performed at an accelerating voltage of 20 kV and a working distance of 15 mm.

X-ray Diffraction (XRD) analysis

XRD analyses of a limited number of carbonate scale samples from the Aberfeldy wells were carried out with a Rigaku Geigerflex Power Diffractometer with a Co tube and a graphite monochromator to filter the K-beta wavelengths. Diffraction patterns were matched against the

International Centre for Difraction Data (ICDD) database. The small amounts, and highly dispersed nature of soil carbonates at Edam precluded the use of XRD as a diagnostic tool.

Soil carbonate selection for $\delta^{13}C$ and $\delta^{18}O$ analysis

Two types of soil carbonate samples (e.g., "bulk" and "selected") were prepared for $\delta^{13}C$ and $\delta^{18}O$ analysis. Bulk samples are portions of soil samples that were neither sieved nor pre-concentrated. Samples of rust and carbonate scales collected from the well bores of the Aberfeldy wells were also considered bulk. Selected carbonate samples are small (several milligrams to several tens of milligrams) and consist of pure carbonate (calcite) with only minor visually identifiable impurities, such as single minerals (e.g., quartz, feldspar, and/or clay) and/or lithic clasts. Selected samples were hand picked under a binocular microscope from soil and carbonate/rust scale samples.

Treatment and reaction of samples for $\delta^{13}C$ and $\delta^{18}O$ analysis

Sample cleaning under a binocular microscope was followed by boiling in 5.25 % sodium hypochlorite solution for a minimum of six hours to remove organic matter. Treated samples were soaked and repeatedly washed with distilled water until the pH of the solution reached a neutral value. Then the samples were dried and transferred to glass vials. Samples of soil carbonates collected at the sites contaminated by liquid hydrocarbons were cleaned by soaking and repeatedly washing them in $CHCl_3$ for 12-46 hours, or until no visible changes in the color and/or transparency of the solvent were noted. To remove solvent, samples were dried at 100°C under vacuum for a minimum of 12 hours.

Sample preparation and $\delta^{13}C$ analysis of soil organic carbon

To remove carbonate, soil samples were dried under vacuum at 60°C overnight and were subsequently fumigated with concentrated HCl in a vacuum desiccator following the method of Harris *et al.*, (2001). Treated samples were dried under vacuum, transferred to Pyrex© tubes, sealed, and burned under vacuum at 530°C in the presence of CuO_2 wire, and copper and silver metal stripes. Samples collected at sites where liquid hydrocarbon contamination was suspected were not processed and analyzed. These include all Golden Lake and Aberfeldy samples and a number of samples collected around wells where oil or diesel fuel/solvent contamination was either established or suspected.

Selected SOM samples were also analyzed for $\delta^{13}C$. The selection process involved examination under a binocular microscope and identification of soil carbonate accumulations. Then these accumulations/aggregates were placed in Pyrex© tubes. Several drops of 10 % HCl were added to remove calcite and the tubes were dried at 60°C (without removing the eluent). After adding CuO_2 wire and silver metal, the glass tubes were evacuated overnight, sealed and heated in an oven at 520°C for 8-12 hours. Produced carbon dioxide was cryogenically purified prior to analysis.

Carbonate reaction and stable isotope analysis

Depending on carbonate contents, between 0.02 and 20 grams of bulk soil sample were reacted with 100 % phosphoric acid following the modified procedure of McCrea (1950). In an attempt to minimize the impact of detrital carbonate (dolomite) on the oxygen and carbon stable isotope composition of the samples, bulk and selected samples were reacted for shorter times (1-4 hours). The short reaction time was justified by the small amount of carbonate in the samples and by experimental results that demonstrated that no significant differences is observed in the carbon and oxygen isotope composition of CO_2 produced as at different reaction times (Sharp, Z., University of New Mexico, personal communication). The CO_2 extracted from soil carbonate and SOM, and also the soil CO_2 were all analyzed for $\delta^{13}C$ and $\delta^{18}O$ on a Finnigan Mat 252 Isotope Ratio Mass Spectrometer in a dual inlet mode.

The amount of inorganic (carbonate) or organic carbon of bulk soil carbonate and SOM samples was estimated by weighting the samples and measuring the pressure of CO_2 produced during the reaction with phosphoric acid or during the burning of the samples. The carbon dioxide pressure was then compared to this produced during the reaction of samples of known amounts of carbonate and/or organic carbon.

$\delta^{18}O$ analysis of groundwater, soil moisture and soil CO_2

The oxygen isotope composition of soil water was determined by direct equilibration with CO_2 following the slightly modified technique of McConville *et al.* (1999). Approximately 8 cm^3 of soil sample were placed in an evacuation vessel then the sample was frozen in liquid nitrogen and pumped under vacuum to remove air. Several millilitres of pure CO_2 were transferred into the vessel and the soil was left to equilibrate for twelve hours at 25°C. Stable isotope results were corrected for soil moisture content using the gravimetric soil moisture data obtained from the same sample and a polynomial fit of the data presented in McConville *et al.* (1999).

Water from the saturated zone at Edam was collected from aluminum tubes installed in the soil near the A3 and A4 wells for the purpose of measuring soil density and moisture with a neutron probe. Water was collected with a sterile disposable PVC downhole bailer and was transferred to pre-cleaned glass vials with screwed tops and Teflon septa. Approximately 5 ml of sample was equilibrated with CO_2 following the method Epstein and Mayeda (1953). The samples were let to equilibrate at 25°C for at least 12 hours prior to CO_2 collection, purification, and measurement.

Soil pH

Approximately five grams of soil sample were weighted and placed in a Pyrex© beaker. 25 ml of distilled water were added and the sample was sonicated for approximately 1 hour. The pH of the solution was measured using Orion 290A pH meter with an Orion 9107 electrode. The instrument was calibrated using standard solutions prepared from powders supplied by Micro Essential Labs. Reproducibility was within ± 0.002 pH units. Measurements were conducted at 25°C.

Anion chemistry of soil waters

Leachates of a number of soil samples were prepared for analysis of dissolved fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulphate. Approximately five grams of soil were mixed with 10 ml of deionized water in precleaned Pyrex© vials. Samples were then sonicated for 45 minutes and centrifuged at 5000 rpm for the same amount of time. Prior to analysis the leachate was extracted with a HDPE syringe and filtered trough a 0.45 micrometer disposable syringe filter. The filtered leachate was analyzed on a Dionex DX600 ion chromatograph equipped with an AS14A anion column. Detection limits are 0.003 mg/l.

Soil moisture and density measurements

Soil density and volumetric moisture contents at wells A3 and A4 were determined by a neutron probe a total of three times during the fall and winter of 2003. Four aluminum tubes 3 m long and with an internal diameter of 5.0 cm were installed at the two Edam sites at 1.0 and 4.0 m distance from the wells. Boreholes were drilled with a mechanical auger and the tubes were pushed into the soil by hand. Measurements were conducted with a CPN 501 hydroprobe capable of measuring soil moisture and *in situ* wet bulk density. The theory and methodology for measuring soil moisture and density by using slow neutrons is described in detail in Wood and Collis-George (1980). Soil moisture and density contents were determined by using calibration equations specific for the probe used for the measurements. The following equation was used to calculate soil moisture for the CNP 501 probe:

$$\theta_v = 48.6477 \times CR_\theta - 21.6047 \qquad [2\text{-}3]$$

where CR_θ is the ratio of the measured neutron counts for moisture in soil *versus* the neutron counts measured at the surface during each field visit. The following equation was used to calculate bulk soil density:

$$\rho = \left\{ -\ln \frac{\left[\frac{\left[CR_\rho - 6.5713 \right]}{-1.63} \right]}{(-0.4274)} \right\} - \left(\frac{\theta_v}{100} \right) \qquad [2\text{-}4]$$

where CR_ρ is the ratio of the measured neutron counts for density *versus* the neutron counts measured at surface. Both equations were provided by Dr. Carl Mendoza at the Department of Earth and Atmospheric Sciences, University of Alberta.

Gravimetric soil moisture was also determined on most soil samples collected at the two Edam sites while drilling to install the soil gas probes. For this purpose 10 g of soil sample was weighted, placed in a glass vial, and dried overnight at 100°C and under vacuum. The dried sample was weighted and volumetric soil moisture contents were calculated assuming an average soil density $\rho = 1.3$ determined from the neutron probe measurements.

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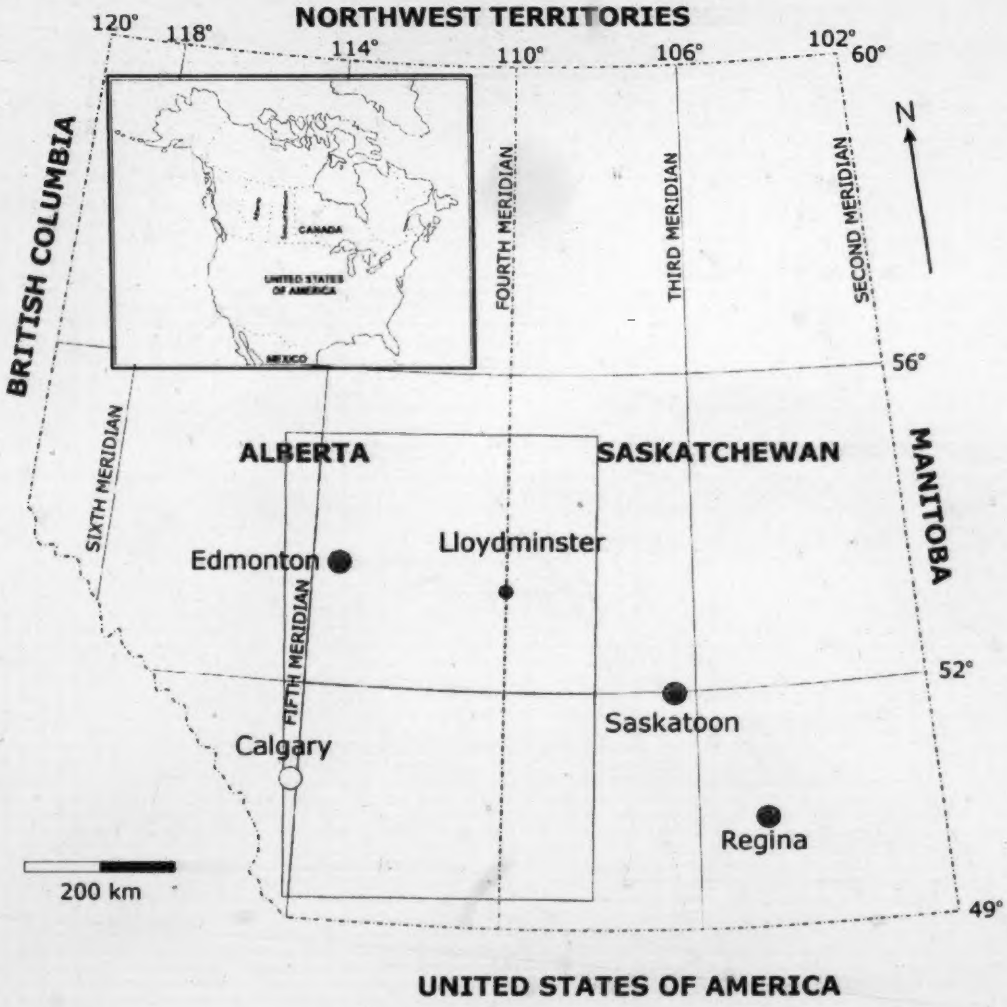
NORTHWEST TERRITORIES
120°
118°
114°
110°
106°
102°
60°
N
BRITISH COLUMBIA
CANADA
UNITED STATES OF AMERICA
MEXICO
FOURTH MERIDIAN
THIRD MERIDIAN
SECOND MERIDIAN
56°
SIXTH MERIDIAN
ALBERTA
SASKATCHEWAN
MANITOBA
Edmonton
Lloydminster
FIFTH MERIDIAN
52°
Saskatoon
Calgary
Regina
200 km
49°
UNITED STATES OF AMERICA

Figure 2-1 Location of the study area (University of Alberta soil and surface casing vent gas database).

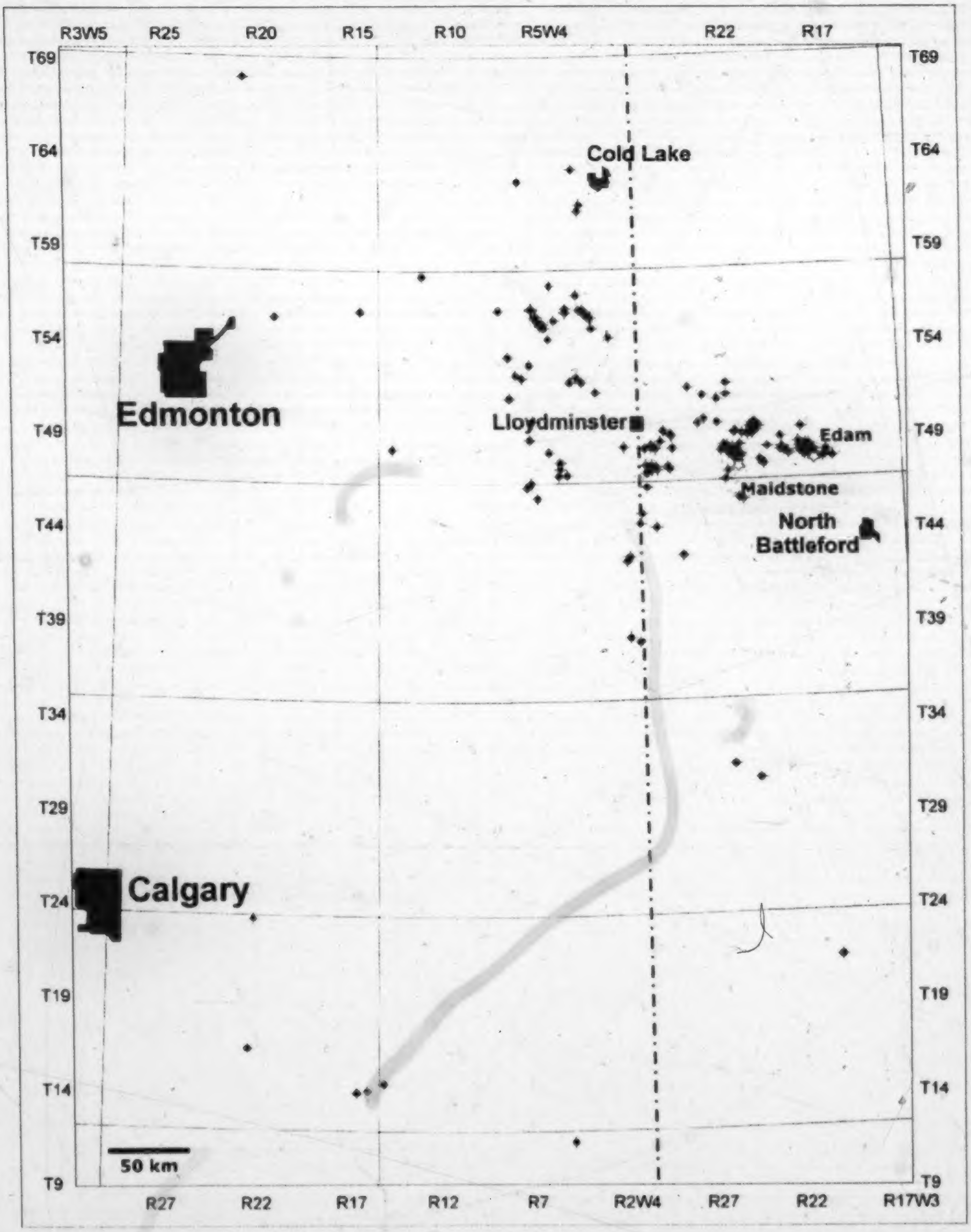
R3W5
R25
R20
R15
R10
R5W4
R22
R17
T69
T64
T59
T54
T49
T44
T39
T34
T29
T24
T19
T14
T9
Cold Lake
Edmonton
Lloydminster
Edam
Maidstone
North Battleford
Calgary
50 km
R27
R22
R17
R12
R7
R2W4
R27
R22
R17W3

Figure 2-2 Enlarged portion of figure 2-1 showing most SCV and SG sample locations (few samples were collected outside this perimeter). The red symbols are gas wells, whereas the green symbols are oil wells. The locations of the two principal research sites Edam and Maidstone are also shown.

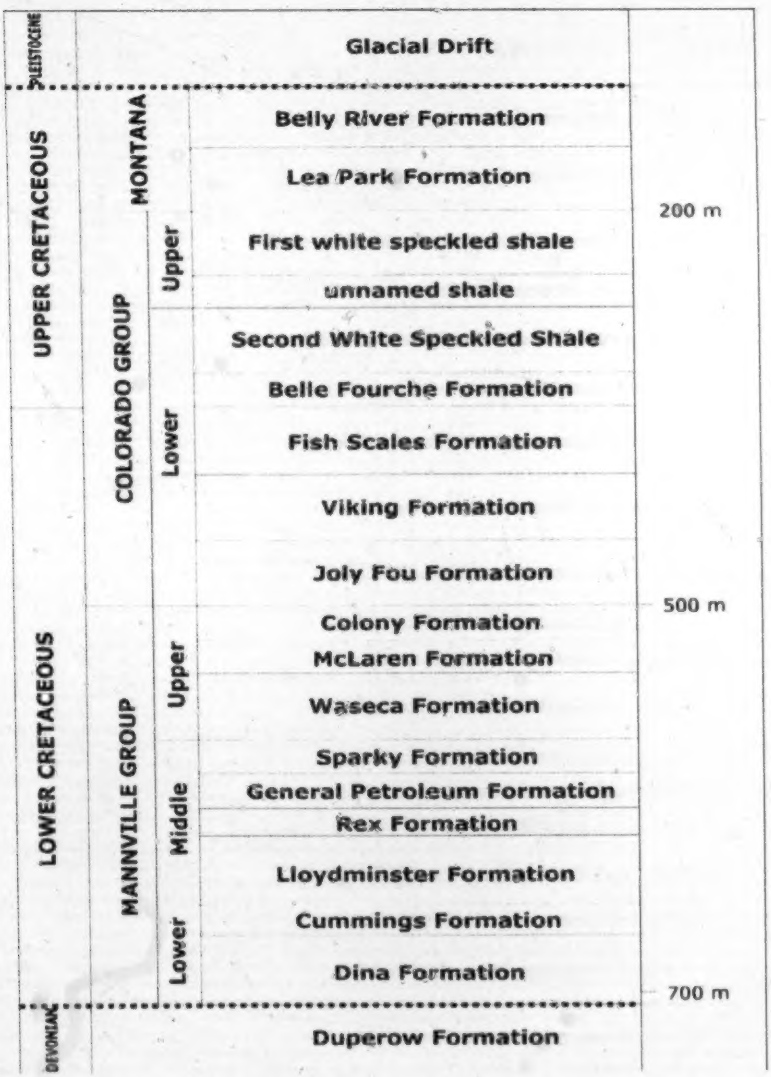
PLEISTOCENE
Glacial Drift
UPPER CRETACEOUS
MONTANA
Belly River Formation
Lea Park Formation
200 m
COLORADO GROUP
Upper
First white speckled shale
unnamed shale
Lower
Second White Speckled Shale
Belle Fourche Formation
Fish Scales Formation
Viking Formation
Joly Fou Formation
500 m
LOWER CRETACEOUS
MANNVILLE GROUP
Upper
Colony Formation
McLaren Formation
Waseca Formation
Middle
Sparky Formation
General Petroleum Formation
Rex Formation
Lloydminster Formation
Lower
Cummings Formation
Dina Formation
700 m
DEVONIAN
Duperow Formation

Figure 2-3 Stratigraphy of the Cretaceous sedimentary rocks in the Lloydminster Area (modified after Orr *et al.* 1977, Virgass, 1977, Leckie *et al.*, 1994, and Hayes *et al.*, 1994).

Figure 2-4 Gravel cover at a suspended well 2D8-11-048-23W3 (Maidstone, Saskatchewan). Topsoil at the well sites if often replaced by sand and gravel to facilitate access to the lease.

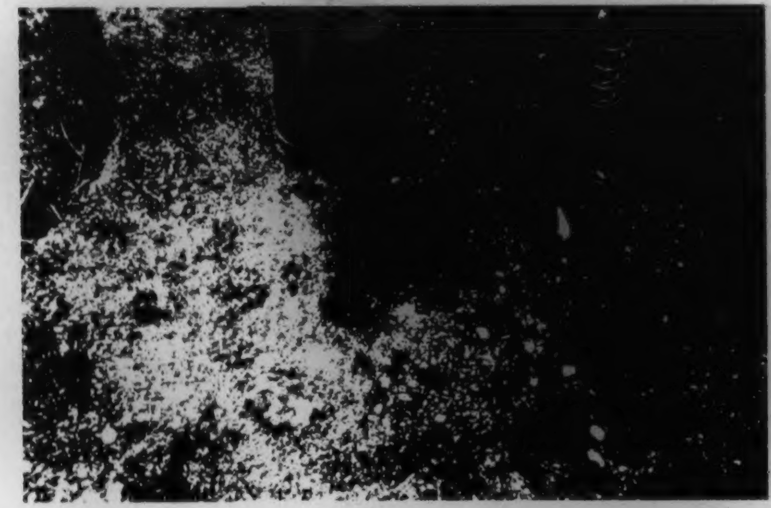

Figure 2.5 Heavy oil contamination in the subsurface at well A10, Maidstone research site.

Figure 2.6 Monitoring site A3, Edam oil field. Scarce vegetation at the site is due to the high sand content of the soil.

b)

Figure 2-7 Abundant vegetation near well A4. The wellhead of A4 is located in a small depression ca. 0.8 m below average soil level.

Table 2-1 Locations of the soil gas probes at the monitoring sites.

A3-17-048-19W3M			A4-17-048-19W3M			A10-11-048-23W3M		
probe	dist. (m)	depth (m)	probe	dist. (m)	depth (m)	probe	dist. (m)	depth (m)
A1	0.30	1.00	A11	0.30	1.00	GA1	0.30	1.00
A2	2.00	1.00	A12	1.00	1.00	GA2	1.00	1.00
A3	4.00	1.00	A13	2.00	1.00	GA3	2.00	1.00
B1	0.30	1.85	A14	4.00	1.00	GA4	4.00	1.00
B2	2.00	1.85	B11	0.30	1.30	GA5	6.00	1.00
B3	4.00	1.85	B12	1.00	1.85	GA6	8.00	1.00
C1	0.30	0.20	B13	2.00	1.85	GA7	12.00	1.00
C2	2.00	0.20	B14	4.00	1.85	GC1	0.30	0.20
C3	4.00	0.20	C11	0.30	0.20	GC2	1.00	0.20
			C12	1.00	0.20	GC3	2.00	0.20
			C13	2.00	0.20	GC4	4.00	0.20
			C14	4.00	0.20	GC5	6.00	0.20
						GC6	8.00	0.20

Table 2-2 Standard deviation of compound specific isotope analyses of C_1 to C_5 gases and CO_2.

Compound	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{iC5}$	$\delta^{13}C_{nC5}$	$\delta^{13}C_{CO2}$
Std. deviation (± ‰)	0.07	0.5	0.3	0.5	0.9	0.9	0.8	0.3

Chapter 3
Fate of leaking natural gas in soils

Introduction

More than three hundred thousand oil and gas wells have been drilled in the Western Canada Sedimentary Basin (WCSB) since the discovery of oil in the beginning of the last century. To prevent cross-formation flow of hydrocarbons and produced water most wells are cemented to surface. However, incomplete cementing due to loss of circulation and/or failure to remove drilling fluid from the well bore often leads to natural gas leakage (Woloschuk *et al.*, 1986; Rich, 1995; Erno and Schmitz, 1996). Gas migrates through annuli between the cement and well casing, or through sub-vertical fractures in the surrounding rocks (Chilingarian *et al.*, 2003). Although the introduction of better cement mixtures and techniques has been successful in reducing leakages, at least one half of the resource wells in the heavy oil district of Alberta and Saskatchewan, and perhaps one third of all wells in Western Canada, are impacted with unwanted surface casing vent (SCV) flow and/or soil gas migration (Erno and Schmitz, 1996; Muehlenbachs, unpublished data). Conservative estimates based on the study of Erno and Schmitz (1996) and unpublished data (i.e., Muehlenbachs), indicate that every year leaking wells contribute approximately 40000 tonnes of natural gas (predominantly methane) to the atmosphere.

Methane is the second most important greenhouse gas, responsible for ca. 20 % of the total greenhouse gas build-up (Whalen, 2005). Although atmospheric concentrations of CH_4 are negligible, on a molar basis CH_4 traps 21 times more heat than CO_2 (Whalen, 2005). Ice core samples demonstrate that human influence on CH_4 concentrations is difficult to detect amongst the natural noise before the year 1800 (IPCC, 1994). In contrast, about 70 % of the atmospheric CH_4 today is of anthropogenic origin (IPCC, 2001). Anthropogenic sources of CH_4 include the coal, petroleum and natural gas industries (18 %), rice paddies (13 %), domestic animals (19 %), sewage treatment (4 %), landfills (7 %), and biomass burning (7 %; Whalen, 2005). Natural sources such as wetlands, termite digestion, and the oceans account for the remaining 32 % of methane emissions to the atmosphere.

It takes about 12 years until ca. 60 % of CH_4 introduced to the atmosphere is removed. In contrast, reduction of the amount of CO_2 that would have an equivalent impact on radiative forcing would require between 50 and 200 years (IPCC, 1995, 2001). Therefore, targeted reduction of CH_4 is expected to have a more rapid impact on global climate than CO_2 reduction (IPCC, 2001). The most important natural sink for atmospheric CH_4 is the troposphere. There CH_4 is oxidized by hydroxyl (OH^-) molecules or broken down by ultraviolet light. Aerated non-agricultural soils comprise another sink for atmospheric CH_4 (ca. 5 %). The studies of Rowe (1998) and Erno and Schmitz (1996) and Arkadakskiy *et al.* (2002) demonstrate that leaking gas is oxidized in soil near the wells. Thus, a better understanding of the factors that control microbial oxidation of CH_4 in soils near the leaking wells in Western Canada is needed.

Current regulations in Alberta require the elimination of all SCV gas leaks that are deemed "serious", i.e., if leaking rates exceed 300 m^3/day, and also if leaking gas may enter shallow aquifers, or if it contains H_2S (EUB, 2003). Gas leaks must also be eliminated prior to lease abandonment (EUB, 2003). Although effective methods for stopping gas leakages exist, success depends upon finding the source of leaking gas along the well bore (Woloschuk *et al.*, 1986; Rich, 1996; Saponja *et al.*, 1996). Standard wireline logging methods had limited success in identifying leaking gas sources (Woloschuk *et al.*, 1986). Since 1995, however, the sources of SCV gases are successfully identified at the University of Alberta, using a comparison between the carbon stable isotope compositions ($\delta^{13}C$) of leaking gases to those of gases extracted from drilling fluids collected while drilling oil and gas wells (Rich, 1995; Rowe, 1998, Rowe and Muehlenbachs, 1999a). Attempts to determine the sources of migrating soil gases using $\delta^{13}C$ compositions have met little success. Preliminary data demonstrated that the $\delta^{13}C$ of hydrocarbon gases from the soil gas samples are often modified significantly by bacterial oxidation and/or methanogenesis (Muehlenbachs, unpublished data).

Microorganisms oxidize CH_4 in both aerobic and anaerobic environments (Whiticar, 1999; Hinrichs *et al.*, 1999). Aerobic oxidation of CH_4 occurs in aerated soils and shallow aquifers and it is mediated by methanotrophic bacteria classified into types I and II on the basis of their carbon metabolic pathway, DNA, and phospholipid fatty acid (PLFA) composition (Hanson and Hanson, 1996; Wise *et al.*, 1999). Aerobic oxidation involves several steps that result in the generation of intermediate compounds such as methanol, formaldehyde and formic acid (Hanson and Hanson, 1996):

$$CH_4 + O_2 \rightarrow CH_3OH \rightarrow HCHO \rightarrow HCOOH \rightarrow CO_2 \qquad [3\text{-}1]$$

The process is catalyzed by both the particulate and the soluble forms of the methane monooxygenaze (MMO) enzyme that is unique to methanotrophic bacteria. Bacteria that produce soluble MMO (sMMO) receive considerable attention because of their ability to catalyze the oxidation of a broad variety of organic pollutants, including halogenated hydrocarbons (Wise *et al.*, 1999; Scheutz *et al.*, 2004). In contrast, anaerobic oxidation of CH_4 is common in the soft sediments on the ocean floor and it is mediated by a syntrophic consortium of hydrogen-consuming, sulphate reducing bacteria and methanogenic archaea working in reverse (Hinrichs *et al.*, 1999; Boetius *et al.*, 2000).

Methanogenesis involves three groups of microorganisms: the hydrolytic fermentative bacteria, the syntrophic acetogenic bacteria, and the methanogenic archaea (Whalen, 2005). Fermentative bacteria hydrolyse complex organic compounds (i.e., carbohydrates, proteins, lipids) to simpler molecules such as acetate, long chain fatty acids, CO_2, and H_2. Acetogenic bacteria oxidize the fatty acids that cannot be metabolized by the methanogens (e.g., propionate and/or butyrate) to acetate, H_2 and/or CO_2, and formate. The latter are the substrates that support the metabolism of the methanogenic archaea (Lovely and Chapelle, 1995). There are two reaction pathways utilized by methanogenic archaea. Acetoclastic methanogenesis involves conversion of acetate to CO_2 and CH_4, whereas carbonate reduction produces CH_4 at the expense of CO_2 and/or HCO_3^-. The first pathway produces 70 to 90 % of all methane in fresh water environments (Groot *et al.*, 2003).

The $\delta^{13}C$ of reactants, products, and intermediate compounds are well suited to study the nature of a wide variety of bacterially mediated processes (Hayes, 2001). Bacterial oxidation of CH_4 to CO_2 is an energy driven unidirectional process. Bond(s) between molecules that contain the light carbon isotope (i.e., ^{12}C) have slightly lower vibration energy and are easier for the microorganisms to cleave (cf. Hayes, 2001). As a result CH_4 oxidation produces a measurable enrichment of the reactant and a concomitant depletion of the product with the heavy carbon isotope ^{13}C (Barker and Fritz, 1981). The kinetic isotope fractionation values associated with this process, determined from field and incubation studies, are used to estimate local and global sources and sinks of CH_4 in both marine and terrestrial environments (Coleman *et al.*, 1981; Whiticar, 1999; Tyler *et al.*, 1994; Happell *et al.*, 1994; Czepiel *et al.*, 1996; Borjesson *et al.*, 2001; amongst others). Reported fractionations, however, vary considerably, which introduces a great deal of uncertainty in those estimates. Variability is attributed to either physical (i.e., diffusion; Tyler *et al.*, 1994) or metabolic processes (Jahnke *et al.*, 1999). Significant temperature dependent variability of the isotope fractionation factors reported by some studies (i.e., Coleman *et al.*, 1981; Tyler *et al.*, 1994; Chanton and Liptay, 2000; Borjesson *et al.*, 2001) is consistent with bacterial metabolism as a principal cause of kinetic fractionation at high CH_4 concentrations. In a recent paper Templeton *et al.* (2006) report that isotope fractionations observed in incubation experiments correlate negatively with measured cell densities. The authors argue that the large spread in fractionation factor values determined from laboratory incubations and natural habitats reflects the impact of ambient conditions on the methanotrophic communities.

Methanogenesis also results in a significant carbon isotope fractionation (Rosenfeld and Silverman, 1959). Bacteriogenic CH_4 has low $\delta^{13}C$ (i.e., less than –55 ‰) and associated CO_2 has $\delta^{13}C$ values from 10 to more than 70 ‰ higher than that of CH_4, depending on whether acetoclastic methanogenesis of carbonate reduction is the dominant pathway, respectively (Whiticar, 1999). Thus, the $\delta^{13}C$ and the concentrations of CH_4 and CO_2 in soil gases can help to identify the principal biologically mediated processes that occur in soil near the wells.

Goals

This chapter has three principal goals: 1) to establish the nature and importance of bacterially mediated processes that occur in soils near the leaking wells; 2) to determine the fraction of CH_4 oxidized (or generated) in soil; 3) to study the impact that environmental factors (i.e., soil temperature, moisture, liquid hydrocarbon contamination, and etc.) have on the different microbial processes.

To achieve these goals the concentrations and/or stable isotope compositions of CH_4 to nC_4H_{10} and/or CO_2, and other non-hydrocarbon gases (i.e., He, H_2) in gas samples from two different data sources were used. The first source comprises a data set of soil and SCV gas samples collected by oil and gas industry service companies and accumulated at the University of Alberta in the last 10 years. Although this database contains gas samples from a number of oil and gas fields in Western Canada, most samples originate from well sites in East-Central Alberta and West-Central Saskatchewan, in an area known as the "heavy oil district" (Chapter 2). Research efforts in the past were focused in this area due to high well density and heightened awareness of gas migration (Rowe and Muehlenbachs, 1999a). The second source of data consists of a large number of soil gas samples collected and analysed in the course of this project. The samples were collected during the long-term monitoring of the soil gas compositions at three leaking well sites near the towns of Edam and Maidstone, Saskatchewan (Chapter 2).

Despite the large number of soil gas samples in the University of Alberta database, there are limitations to the usefulness of the data. Those include lack of information about how samples were collected, soil type and moisture, presence/absence of liquid hydrocarbon contamination, and missing sampling dates and analytical data. Therefore, this chapter is divided into two parts. The first part is concerned with interpreting data from the University of Alberta database, whereas the second focuses on results from the long term monitoring at the three field sites.

Part I

Soil and SCV gas sample compositions from the University of Alberta database

Results

The concentrations of hydrocarbon and non-hydrocarbon gases and the $\delta^{13}C$ compositions of hydrocarbon gases and CO_2 from the SCV and soil gas samples from the University of Alberta database are presented in Appendices 1 and 2. A statistical summary is also presented in Table 3-1.

Non-hydrocarbon gases

Helium concentrations reach 6500 ppmv with both the highest and average values much higher in the SCV group (Table 3-1). Hydrogen concentrations are also available for a limited number of gas samples. SCV gases contain as much as 1960 ppmv of hydrogen and have average concentrations higher than those of soil gases (Table 3-1). Although CO_2 concentrations are not available for the SCV gas samples included in Appendix 1, measured $\delta^{13}C_{CO_2}$ values indicate that many gas samples contain at least 100 ppmv of CO_2, which is the detection limit of the GC-CF-IRMS. Some SCV gas samples from the University of Alberta data base, not included in this study, contain as much as 1.9 % v/v CO_2 (Muehlenbachs, unpublished data). Soil gas samples, however, contain significantly more CO_2, with average concentrations of 3 % v/v and values as high as 16 % v/v (Table 3-1).

Methane and C_2+ gases

Methane is the predominant (>90 % v/v) hydrocarbon gas in soil and SCV gas samples. The lower average concentration of CH_4 and other gaseous hydrocarbons in soil gas samples (e.g., Table 3-1; Fig. 3-1a, b) may result from a combination of factors including atmospheric air contamination, and bacterially mediated oxidation. The C_2+ gas content of both soil and SCV gases is negligible (i.e.,

<0.3 % v/v; Table 3-1). The ratio of C_1 to ($C_1+\Sigma C_2+$), termed gas "wetness" index, is often used to distinguish between natural gases of bacteriogenic and thermogenic origin (cf. Whiticar, 1999). Due to small numerical differences in the "wetness" indices of the Colorado and Montana Group gases determined in this study, another formulation (i.e., $C_1/\Sigma C_2+$) is used instead. The $C_1/\Sigma C_2+$ ratio of both soil gas and SCV samples is highly variable (i.e., 3 to 3700 for SCV gases and 13 to 98000 for soil gases). Soil and SCV samples that contain more than 50 % v/v CH_4 exhibit much less variability, however (Fig. 3-2).

Carbon stable isotope compositions

The $\delta^{13}C$ of methane in the SCV group is less variable and it is on average 5 ‰ lower than the $\delta^{13}C_{CH4}$ of soil gases (Table 3-1; Fig. 3-3a, b), and $\delta^{13}C_{CH4}$ compositions in both groups are skewed towards higher and, to a much lesser extent, lower values (Fig. 3-3a, b). The $\delta^{13}C$ of the C_2+ gases exhibit less variability than that of methane (Table 3-1). Similarly to methane, the $\delta^{13}C$ compositions of C_2+ gases in the soil gas group of samples deviate towards heavier values at low total gas concentrations indicating that C_2+ gases are also oxidized by soil bacteria (Fig. 3-4). Carbon isotope fractionation of the light hydrocarbon gases becomes progressively smaller with increasing carbon numbers (Fig. 3-4). The $\delta^{13}C$ of soil CO_2 varies from +10 to -92 ‰ and the average $\delta^{13}C$ value is lower than the average $\delta^{13}C_{CO2}$ of CO_2 from the SCV group (Table 3-1). Soil gases also exhibit a weak bimodal distribution of their $\delta^{13}C_{CO2}$ with peaks at about -35 and -25 ‰, respectively. In contrast, most SCV gases contain CO_2 that has $\delta^{13}C$ compositions between -10 and -25 ‰ (Fig. 3-5a, b).

Discussion of Part I

Non-hydrocarbon gases

The CH_4/He ratios of SCV gas samples from the University of Alberta database vary from 130 to 7000. The latter value, however, is an outlier and originates from one of the samples that contains less than 3 % v/v of methane. Low CH_4 concentrations imply low flow rates and advection likely comparable to or slower than the rate of diffusion that will result in selective helium loss (see discussion in Part II). With the exception of the value in question, the CH_4/He ratios of the SVC gas samples vary between 130 and 1500. The latter fall within the range of ratios calculated from the He and CH_4 contents of the Western Canada gas samples of Hiyagon and Kennedy (1992; e.g., 53 to 11000), but exhibit much less variability. With the exception of two samples that contain less than 3 % v/v of methane, the CH_4/He ratios of the rest of the SCV samples, for which helium data is available, exhibit a negative correlation ($R^2 = 0.53$) with the $\delta^{13}C$ of ethane. This correlation suggests that less hydrocarbon gas of thermogenic origin was generated in the Colorado Group sedimentary formations that are less mature. The CH_4/He ratios of the few soil gas samples, for which helium measurements are available, vary from 70 to 300000. The very high values most certainly reflect preferential loss of helium in the soil. The lack of correlation between the CH_4/He ratios of soil gases and the $\delta^{13}C$ of ethane in the soil gas group is also explained by a combination of preferential He loss and the kinetic isotope effect (KIE) of bacterial oxidation of ethane in soil (see below).

In contrast to helium, hydrogen concentrations in the SCV and soil gas groups show no correlation with CH_4. Hydrogen is highly reactive and mobile and thus uncommon in aerated soils and sedimentary basins. Only small amounts (e.g., <1 %) are found in natural gas reservoirs (Jenden *et al.*, 1988). Surprisingly, some SCV gas samples collected at recently cemented wells contain very high amounts of H_2 (i.e., tens of percents; Muehlenbachs, unpublished data; Szatkowski, personal communication, 2005). Elevated pressures measured at some of those surface casing vents were even considered evidence for gas leakage (Szatkowski, personal communication, 2005). Both the gas pressure and the hydrogen concentrations at those wells, however, abated significantly and/or disappear completely after several weeks (Szatkowski, personal communication, 2005).

Hydrogen is produced in both inorganic (i.e., electrochemical) and microbially mediated reactions. Electrochemical production of H_2 may occur along the steel casings of the wells, if these transect sediments/soils of variable moisture and dissolved ion concentrations and/or pH. Alternation of soils and sediments of contrasting resistivity (e.g., sand/gravel) may also generate a galvanic potential that will result in H_2 production (Almardy, 1999). Hydrogen is also produced when OH^- groups in fresh cement come into contacts with the zinc oxide coating of the steel casings (American Galvanizers' Association, 2004), which is the most likely explanation for the high hydrogen content of SCV gases collected from recently cemented wells, and also explains why H_2 concentrations drop significantly after time.

Biologically mediated H_2 production involves a consortium of fermentative, acetogenic, and methanogenic microorganisms (Mormile *et al.*, 1996). The most likely substrates used by the fermenting bacteria in the deep subsurface are intermediate compounds and end-products of the aerobic and/or anaerobic oxidation of liquid hydrocarbons (e.g., alcohols, fatty acids and etc.; Dimitracopoulus and Muehlenbachs, 1987). Formation of suitable substrates, however, requires introduction of O_2 or other electron acceptors, either through loss of drilling fluid or through the injection of surface water to enhance heavy oil recovery. However, most leaking wells in the Lloydminster area were drilled tens of years ago and it is thus unlikely that electron acceptors supplied through drilling fluid leakages are still available in the sediments around the well bore. In addition, the low permeability of the Colorado Group shales renders large scale invasion of water of external origin unlikely. Therefore, elevated hydrogen concentrations in most SCV gas samples likely reflect electrochemical hydrogen production along the well casings.

Although the average hydrogen concentration in the soil gas group is lower, gas samples collected at a number of sites contaminated with oil have elevated H_2 concentrations. Samples collected near wells 2D8-11-048-23WM, B11-12-048-23W3M and especially near the Maidstone monitoring site are good examples (Appendix 2). Elevated H_2 contents were also measured in the soils at the two Edam sites where there is no oil contamination in the soil.

Carbon dioxide in concentrations as high as 17200 ppmv (average 2800 ppmv) is detected in a number of production gas samples from the Colorado Group shales (Muehlenbachs, unpublished data). Both the concentrations and $\delta^{13}C_{CO2}$ are used to determine the origin of CO_2 in natural gas reservoirs (Wycherley *et al.*, 1999). Large amounts of CO_2 (e.g., >10 %) usually have $\delta^{13}C_{CO2}$ compositions between 0 and -10 ‰ and are thus considered of inorganic (metamorphic, mantle, marine carbonate dissolution) origin. In contrast, small amounts of CO_2 (<10 % v/v) of variable $\delta^{13}C$ compositions (i.e., +15 to -30 ‰) are considered of biogenic origin (cf. Wycherley *et al.*, 1999). Measured $\delta^{13}C_{CO2}$ compositions of production gas samples from the Colorado Group shales are highly variable (e.g., -3.6 to -45.6 ‰) indicating multiple sources that include bacterial oxidation of methane. The $\delta^{13}C_{CO2}$ compositions of the SCV gas samples exhibit even great variability (i.e., from +1.3 to -73.3 ‰; Fig. 3.5). Although most SCV samples contain CO_2 that has $\delta^{13}C$ between -5 and -20 ‰, compositions in this range are non-unique and indicate that CO_2 in those samples may be a mixture of CO_2 of metamorphic origin, decarboxylation reactions and/or oxidation of organic matter or liquid hydrocarbons (Carothers and Kharaka, 1980). The $\delta^{13}C_{CO2}$ in equilibrium with marine carbonates at formation temperatures (e.g., 30-50°C), is -7 ‰ (Romanek *et al.*, 1992). Therefore, the SCV gas samples may also contain CO_2 in isotope equilibrium with marine carbonates. In fact, given the relatively small amounts and highly reactive nature of CO_2, an isotope exchange with HCO_3^- from water in contact with cement from the annular space between the well bore and the well casing could be responsible for the carbon isotope compositions of some CO_2 samples. The low $\delta^{13}C$ of CO_2 (e.g., as low as -73.3 ‰) of a small number of gas samples collected from both surface and production casings indicate that bacterial oxidation of natural gas occurs either in the gas reservoirs or in the casings. The lowest $\delta^{13}C$ values are measured in SCV samples that have the lowest CH_4 concentrations, thus, reinforcing the hypothesis that bacterial oxidation of CH_4 occurs within the surface casings of some wells. The low total hydrocarbon gas concentrations at these wells imply low flow rates. Low leaking rates would allow air to enter the surface casing thus enabling aerobic methanotrophy. Values higher than -5 ‰ are also measured in a few SCV gas samples indicating that methanogenesis by carbonate reduction occurs either in the subsurface or in the casing.

The variability of $\delta^{13}C$ compositions in the soil gas group is greater than the variability in the SCV gas group. The low average $\delta^{13}C_{CO2}$ of the soil gas samples indicates that bacterial oxidation of gaseous and liquid hydrocarbons is the principal sources of soil CO_2 (Fig. 3-5). Values as high as +10 ‰ however, demonstrate that methanogenesis (via carbonate reduction) likely occurs in soil at a number of well sites. Presence of soil respired CO_2 in the soil gas samples is also likely, especially in samples collected during the active growing season at abandoned well sites with abundant vegetation.

Photosynthetic uptake of atmospheric CO_2 (e.g., $\delta^{13}C$ ca. –8 ‰) is accompanied by a significant ^{13}C depletion. The C_3 and C_4 plants fractionate carbon stable isotopes by 20.0 and 5.5 ‰, respectively (Chapter 5) and heterotrophic bacterial oxidation of soil organic matter (SOM) produces CO_2 of carbon isotope composition similar to that of SOM (Clark and Fritz, 1997). When the impact of CO_2 diffusion in soil is added (e.g., ca. 4 ‰) the $\delta^{13}C$ of soil CO_2 produced from the oxidation of SOM should have average $\delta^{13}C$ values of ca. –24 ‰ (C_3) and –9 ‰ (C_4 plants), respectively (see Chapter 5). Unfortunately, CO_2 produced from the decarboxylation of kerogen of C_3 plant origin and the bacterial oxidation of heavy oil (i.e., ca. -30 ‰; Ringham, 1981) has $\delta^{13}C$ values that overlap with those of CO_2 produced by soil respiration. This renders the identification of CO_2 from those two sources difficult, especially at low CO_2 concentrations.

Methane and C_2+ gases

Significant spread towards higher, and to a lesser extent, lower $\delta^{13}C$ compositions of methane from the SCV and soil gas samples is observed at low CH_4 concentrations (Fig. 3-6). The spread towards higher $\delta^{13}C$ values reflects the impact of the kinetic isotope effects related to bacterial oxidation, whereas the spread towards lower $\delta^{13}C$ values indicates the presence of methane of either bacteriogenic or immature thermogenic origin. The magnitude of the kinetic isotope fractionation between methane and carbon dioxide (i.e., $\varepsilon_{CH4-CO2}$) helps to establish the nature of the biological processes that occur in soil near the leaking wells (Hayes, 2001):

$$\alpha_{CH4-CO2} \approx \left(\frac{1000 + \delta^{13}C_{CH_4}}{1000 + \delta^{13}_{CO_2}} \right) \qquad [3\text{-}2]$$

$$\varepsilon_{CH4-CO2} \approx 1000\,(\alpha - 1)$$

Values for $\varepsilon_{CH4-CO2}$ are rarely determined in both natural and incubation studies due to complications related to the acquisition of representative $\delta^{13}C_{CO2}$ data (i.e., the presence of sources of CO_2 other than methanotrophy). Fractionation factors are thus most commonly estimated from the $\delta^{13}C_{CH4}$ compositions of the initial and residual methane and the fraction of methane oxidized (Coleman *et al.*, 1981; Borjesson *et al.*, 2001, amongst others). However, information about the initial $\delta^{13}C_{CH4}$ composition and estimates of the fraction of CH_4 oxidized in soils near the leaking wells is difficult, if not impossible, to acquire because of the impact of bacterially mediated reactions and sample dilution. Therefore, fractionation factors at the leaking well sites can only be approximated by using the $\delta^{13}C$ compositions of coexisting CH_4 and CO_2. This method is likely to produce erroneous results because the presence of soil CO_2 and CH_4 of unrelated origin (i.e., soil respiration, bacterial oxidation of liquid hydrocarbons) cannot be precluded. Despite these shortcomings, an attempt was made to evaluate the nature of the biological processes in soil near the leaking wells by plotting the $\delta^{13}C$ compositions of the SCV and soil gases on a CH_4 vs. CO_2 diagram (Whiticar, 1999; Fig. 3-7). The apparent $\varepsilon_{CH4-CO2}$ values of the soil gases vary significantly from -73[2] to +31, whereas for SCV gases these values vary from -65 to +10. The diagram demonstrates that the soil group contains a much larger number of samples having $\varepsilon_{CH_4-CO_2}$ values in the -30 to +40 range. These values are consistent with oxidation of gaseous and liquid hydrocarbons in soil occurring at a large number of sites. Only a comparatively small number of samples exhibits "positive" $\varepsilon_{CH_4-CO_2}$ indicating that CH_4 is the predominant or sole source of CO_2 carbon. This finding implies that bacterially mediated processes other than methanotrophy are common in soils at a large number of leaking well sites in Western Canada.

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[2] The negative sign is used here to denote apparent $\varepsilon_{CH4-CO2}$ where $\delta^{13}C_{CH4}$ is lower than that of CO_2.

It is worth noting that diagram 3-7 is designed to be used with CH_4 and CO_2 of bacteriogenic origin related by methanogenesis or methanotrophy (Whiticar, 1999). Therefore, it has no applicability for samples that consist of methane and CO_2 not related to either processes (i.e., thermogenically generated gases). Hence, the plotting of a large number of SCV and soil gas samples in the field of "methyl fermentation" is likely coincidental. However, the diagram still helps to identify sites where leaking gases are subjected to bacterial oxidation, and also sites where bacteriogenic methane and/or residual carbon dioxide from bacterial methanogenesis by carbonate reduction are produced. The $\delta^{13}C$ of methane from the Montana and Colorado Group varies between -60 and -70 ‰ (Rowe, 1998). Therefore, only SCV gas samples having apparent $\varepsilon_{CH_4-CO_2} < -65$ are likely to contain CO_2 produced or modified by methanogenesis (e.g., $\delta^{13}C > -5$ ‰).

A comparison between SCV and soil gases collected at the same well sites

To determine if leaking soil and SCV gases have a common source, and to evaluate the impact that bacterial oxidation and temperature variability have on the molecular and stable isotope composition of leaking gas, 47 well sites, where both SCV and soil gas samples were collected, were selected for a comparative study (Table 3-2). In addition to comparing the concentrations and stable isotope compositions of hydrocarbon and/or non-hydrocarbon gases from the SCV and soil gases, the $C_1/\Sigma C_2+$ ratio and the ratios of ethane to propane and the isotope separations between ethane and propane (e.g., $\Delta^{13}C_{ethane-propane}$) of the pairs of SCV and soil gases are also compared.

The comparison reveals the existence of three principal groups of gases (Fig. 3-8). Surface casing vent and soil gases from the first group have the same or very similar $\delta^{13}C$ compositions and molecular ratios (Table 3-2). The second group consists of soil gases that have $\delta^{13}C$ compositions lower than those of SCV gases with some soil gases having molecular ratios that could be significantly different to those of the SCV gases. The third group includes samples collected from sites where hydrocarbon soil gases have higher $\delta^{13}C$ compositions and/or highly variable molecular ratios when compared to the SCV gases.

Group I

SCV and SG gases in this group have remarkably similar isotope compositions and molecular ratios (Table 3-2; Fig. 3-8). In most cases, the $\delta^{13}C$ of CO_2 of the soil gases is lower than that of the SCV gas. A number of soil gases have $\delta^{13}C_{CO2}$ values lower than -30 ‰ indicating that bacterial oxidation of CH_4 contributes to the CO_2 pool. The similar to identical $\delta^{13}C$ compositions and molecular ratios strongly suggest a common origin for the SCV and soil gases at these sites. These also suggest that only a small volume of methane and/or C_2+ gases is oxidized in the soil. Natural gas concentrations in soil at these sites is high (e.g., >20 %). Thus, proximity to the leaking gas sources, high flow rates and low soil air permeability are the most likely reasons why little evidence of bacterial oxidation is seen in these samples. Other factors, such as presence of toxic chemicals or competitive substrates, such as the (by) products of oil degradation that provide more free energy, may also prevent methanotrophy at these sites.

Group II

This group includes soil gas samples that contain one or more light alkane gases with $\delta^{13}C$ compositions lower than those of the SCV gases (Fig. 3-8). The molecular ratios of the soil gases in this group are variable, with values sometimes similar to those of the SCV gases. On the basis of the characteristics listed above, soil gases could be divided into two subgroups. The first subgroup consists of samples having $\delta^{13}C$ compositions of all or most hydrocarbon gases lower than those of associated SCV gases, clearly indicating that SCV and soil gases are of different origin (Table 3-2). In most cases the $C_1/\Sigma C_2$+ ratios and the $\Delta^{13}C_{ethane-propane}$ of soil gases are also different (i.e., higher) indicating that these gases are indeed of lower maturity than the SCV gases collected at the same sites (Table 3-2). The presence of leaking gases of different maturity in the soil and the SCV of the same well indicates that there are at least two sources of leaking gas and that soil gases originate from sedimentary formations above the surface casings of the well, which in the Lloydminster area is usually set at vertical depths ranging from 80 to 100 mbs.

The second subgroup includes soil gases that contain only CH_4 and/or ethane of lower $\delta^{13}C$ compositions to those of the SCV gases. This could be due to the addition of CH_4 and/or ethane from bacteriogenic origin, or could be the result of mixing with less mature gases. Although, to the best knowledge of the author, bacterially mediated generation of ethane in soil has not been reported, low concentrations of dissolved ethane of suspected bacteriogenic origin are detected in marine and lake sediments (Whelan *et al.*, 1980). Ethane of low $\delta^{13}C$ composition (e.g., from -45.4 to -73.9 ‰) and suggested bacteriogenic origin is also reported from the Judith River and Milk River aquifers in southern Saskatchewan and Alberta (Taylor *et al.*, 2000). On the basis of their isotope data, Taylor *et al.* (2000) hypothesize that most, if not all, ethane in the shallow aquifers in Western Canada is of bacteriogenic origin, and that a significant portion of the leaking gases must, therefore, be of shallow bacteriogenic origin. However, the average $\delta^{13}C_{ethane}$ of SCV gas samples in Western Canada is -41 ± 7 ‰ (n = 1713; Muehlenbachs, unpublished data). Rowe (1998) and Rowe and Muehlenbachs (1999) demonstrated that these gases are of thermogenic origin. In addition, immature thermogenic gases from the Upper Colorado and Montana Groups extracted from drilling mud and collected from SC vents in Western Saskatchewan and Alberta also contain ethane and n-butane of $\delta^{13}C$ as low as -60 ‰ and -40 ‰, respectively (Rowe, 1998; Muehlenbachs, unpublished data).

Taylor *et al.* (2000) also cite the lack of C_3+ hydrocarbons in the Milk River aquifer samples as a proof that all ethane there is of bacteriogenic origin. However, thermogenic gases of low maturities contain small amounts of C_3+ hydrocarbons that are difficult to detect by standard gas chromatography. Analytical results acquired from gas chromatographs optimized to measure very low (i.e., ppbv) levels of light hydrocarbon gases demonstrate that most natural gas samples colleted from gas wells producing from the Milk River Formation contain measurable amounts of C_3+ hydrocarbons of comparatively low $\delta^{13}C$ compositions and isotope separations indicative of incipient thermogenic gas origin (Muehlenbachs, unpublished data). In addition, incubation studies using anoxic sediment slurries demonstrate that only very small amounts of ethane of apparent bacteriogenic origin are produced from ethylated compounds such as ethanethiol and diethylsulphide (Oremland *et al.*, 1988). Therefore, most of the ethane in the shallow aquifers of western Canada is of thermogenic and not bacteriogenic origin as suggested by Taylor *et al.* (2000).

Mixing of shallow (i.e., Montana group) immature gas that contains small amounts of C_3+ gases with gas or comparatively higher maturity from the lower parts of the Colorado Group will have a negligible impact on the $\delta^{13}C$ compositions of propane and butane of the Lower Colorado end-member. Therefore, it is likely that gases from the second subgroup comprise mixtures of Colorado gases, similar to those in the associated SCV's, and lesser amounts of immature thermogenic gases of Montana and/or Upper Colorado Group origin that have formed *in situ* or migrated to and accumulated in shallow reservoirs located above the surface casings.

Group III

This group contains soil gas samples of significantly lower average hydrocarbon gas concentrations and higher $\delta^{13}C$ compositions to those of associated SCV gases. The difference in the $\delta^{13}C$ of the respective n-alkane gases from the soil and the SCV samples at these sites becomes greater at higher carbon numbers and lower total hydrocarbon gas concentration. In addition, a unique feature that separates this group from the two others is that the molecular ratios of soil gases exhibit seasonal variability allowing further division of Group III gases into two subgroups (see Table 3-2). The first subgroup includes soil gases collected between May and September. Most soil gases in this subgroup have lower $C_1/\Sigma C_2+$ ratios to those of the SCV gases collected at the same sites. Both the C_2/C_3 ratio and $\Delta_{ethane-propane}$ of the soil gas samples are lower too (Table 3-2). The second subgroup includes samples collected from the end of September to the middle of May. The $C_1/\Sigma C_2+$ ratios of soil gases in this group are as much as one order of magnitude higher than the $C_1/\Sigma C_2+$ ratios of the SCV gases at the sites. The C_2/C_3 ratio also increases by as much as 50 % (Table 3-2). In spite of the increasing molecular ratios, the $\delta^{13}C$ compositions and isotope separations (e.g., $\Delta_{ethane-propane}$) of those soil gases trend towards higher values like those of most gases in the summer subgroup.

Seasonal variability of the $C_1/\Sigma C_2+$ ratios of soil gas samples indicates that processes that depend on soil temperature are the most likely reasons for decoupling CH_4 from the rest of the light hydrocarbons. Low $C_1/(\Sigma C_2+)$ ratios in the summer indicate that CH_4 is preferentially oxidized in the warmer part of the year. There are, however, several possible explanations as of why the $C_1/(\Sigma C_2+)$ ratios of the soil gases increase in the winter. One possibility is addition of bacteriogenic methane. However, metabolic rates of methanogenic archaea slow down significantly below 5°C (Whalen, 2005). Field observations and temperature measurements at the monitoring sites also indicate that soil to 1.0 mbs is completely frozen from Mid October/November to late April and/or the first part of May (Table 3-3). Therefore, it is improbable that bacterial methanogenesis capable of providing enough methane to significantly modify the $C_1/(\Sigma C_2+)$ ratio occurs at that time of the year. Second possibility is that C_2+ hydrocarbons are preferentially oxidized in winter. If preferential oxidation of C_2+ occured, the $\delta^{13}C$ compositions of the residual C_2+ gases should have been enriched significantly in ^{13}C. The $\delta^{13}C$ values of C_2+ soil gases collected in the winter, however, do not appear to have $\delta^{13}C$ values significantly higher than those in samples collected in the summer (Table 3-2). The above does not preclude the possibility that the $C_1/\Sigma C_2+$ ratio increases, not because C_2+ gases are preferentially oxidized, but because rates of CH_4 oxidation slow down relative to those of C_2+ gas oxidation.

The third possibility is that CH_4 is separated from the rest of the hydrocarbon gases due to differences of the physical properties of the n-alkane gases. A review of those properties reveals that observed large variation of the iC_4/nC_4 ratio in winter is apparently due to differences in the boiling temperatures of the two isomers. While the boiling temperature of n-butane is 0.6°C, iso-butane boils at -11°C. Therefore, when soil temperatures are close to or lower than freezing, condensation of n-butane in the soil pores in the upper parts of the soil profile is expected, which is likely the reason why n-butane concentrations decrease significantly in winter. Although boiling temperatures of the rest of the C_2+ gases are lower than that of n-butane, it is nevertheless possible that C_2+ gases may partition into the liquid n-butane phase, which would explain the increasing $C_1/\Sigma C_2+$ ratios observed in winter.

Summary and conclusions of Part I

A review of the concentrations and $\delta^{13}C$ compositions of light hydrocarbon SCV and soil gas samples collected in the last 10 years at the University of Alberta demonstrates that microbial oxidation of liquid and gaseous hydrocarbons is a common microbially mediated process in soils near the leaking wells of Western Canada. The high, variable $\delta^{13}C$ compositions of CO_2 from the SCV and soil gas samples indicate that acetoclastic methanogenesis also occurs in soil near a number of wells. A statistically significant correlation between the CH_4/He ratios and $\delta^{13}C$ of ethane in SCV gas samples also suggests that the Colorado Group shales of lower maturity contain less hydrocarbon gas of thermogenic origin. Potential electrochemical origin of elevated hydrogen concentrations observed in SCV gas samples should be of concern to the oil industry, because of the ability of hydrogen gas to cause metal embrittlement.

The molecular and carbon stable isotope compositions of light hydrocarbon gases from SCV and soil gas samples demonstrates that at a number of leaking well sites these are of different origin or comprise mixtures of gases of different sources and/or origin. The latter has serious implications for the oil industry and regulatory agencies in Western Canada because in attempts to remediate leaking wells are almost always based on the $\delta^{13}C$ of a single gas sample that, for most part, originates from the SCV of the well. Results also demonstrate that if soil samples contain less than 20 % v/v methane, their $\delta^{13}C$ compositions are likely to be impacted by bacterial oxidation and thus cannot be used to trace the origin of leaking gas.

Part II

Results from the monitoring sites at Edam and Maidstone

Non-hydrocarbon gases

Helium concentrations in soils near the leaking wells vary from 1500 ppmv in probes proximal[3] to the source of leaking gas to <12 ppmv in the distant and background probes[4]. He concentrations in gas samples collected from the proximal probes at all three wells follow a similar trend suggesting that leaking gas flow at these sites is close to steady state (Fig. 3-9). Oxygen concentrations in the soil gas samples vary from near atmospheric values, measured in background soils and in soils away from the wells, to as low as 300 ppmv in small domains close to the sources of leaking gas, where the proximal probes are installed. Those domains are surrounded by larger O_2-deficient areas that may reach several metres in diameter. Those areas have (significantly) lower than atmospheric O_2 concentrations (e.g., <4 % v/v in the summer and ca. 8 % v/v in winter; Figures 3-10 and 3-11) and are hereafter referred to as microaerophilic[5] zones.

The hydrogen content of soil gases vary from below detection to 5500 ppmv with soil gases collected at well A10 having the highest concentrations (Table 3-1). Elevated H_2 is detected in microaerophilic soil at Edam only in the summer (Appendix 3). In contrast, hydrogen concentrations in the microaerophilic soil near well A10 increase by several orders of magnitude in winter. The seasonal variability suggests that H_2 production at both sites is related to biological processes. Carbon dioxide concentrations in the proximal probes near the three wells are generally low throughout the monitoring period (e.g., <1000 ppmv). Increase of CO_2 concentrations to as much as 10000 ppmv is observed only at well A3 in the second half of the period (Fig. 3-12). Higher (e.g., >20 % v/v) amounts of soil CO_2 are measured in the microaerophilic and oxygen-rich soil near the wells.

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[3] The closest soil gas probes to the source of leaking gas at the three sites are referred to as proximal.
[4] For soil gas probe locations, please refer to Table 2-1, Chapter 2.
[5] The term "microaerophilic" used here describes areas in the soil where O_2 concentrations are (significantly) lower than these expected at the same depth in soil away from a leaking well.

Methane and C_2+ gases

Methane concentrations vary from 100 % v/v in the proximal probes, to below detection in the oxygen-rich soil (Table 3-1; Figures 3-13 to 3-16). The distance at which CH_4 is detected in soils roughly overlaps with the outline of the microaerophilic zones. The C_2+ concentrations in soil gas near the three wells follow a distribution pattern where C_2>C_3>iC4>nC4. Reversals, however, are not uncommon, especially at low hydrocarbon gas concentrations. Like methane, C_2+ concentrations decrease rapidly away from the leaking gas sources. The $C_1/\Sigma C_2$+ ratios in soil gases collected from the proximal probes at the two Edam wells overlap (e.g., 387 ± 40 for A3 and 403 ± 30 for A4). Soil gas collected at well A10 has a lower $C_1/\Sigma C_2$+ ratio (e.g., 272 ± 20) indicating that leaking gas sources at Edam and Maidstone are different. The $C_1/\Sigma C_2$+ ratios of the soil gases in the microaerophilic and the O_2 rich soils exhibit extreme variability. Values as high as 63000 and as low as 0.3 are measured in gas samples of very low total hydrocarbon gas content. The $C_1/\Sigma C_2$+ ratios of gases in microaerophilic and O_2-rich soils exhibit seasonal variability with high values measured in winter and low in summer (Figures 3-17, 3-17, and 3-19). The concentrations of C_6+ gases in soil samples collected at the Edam wells are negligible and are not included in this presentation. Gas samples collected in the soil at the A10 site, however, contain as much as 3000 ppmv of C_6+ gases with higher C_6+ concentrations measured in the summer than in the winter.

Carbon stable isotope compositions

The $\delta^{13}C_{CH4}$ in soil gases collected at the three well sites varies from -71.0 to -21.5 ‰ (Appendix 3). The $\delta^{13}C_{CH4}$ of the soil gas increases with decreasing concentrations and increasing distance from the well bore. The largest increase (e.g., 48.1 ‰) is observed at well A3. The $\delta^{13}C_{CH4}$ at wells A4 and A10 vary less (i.e., 37 ‰). Methane (and C_2+ gases) in soil gas samples collected from the proximal probes at the three wells have the lowest $\delta^{13}C$ compositions and exhibit the least variability (Fig. 3-20). An exception is well A3, where a trend towards increasing $\delta^{13}C_{CH4}$ begins in the winter of 2002/2003 and continues throughout the summer of 2003. In the fall of 2003 the $\delta^{13}C$ of CH_4 increases by as much as 11 ‰ (Fig. 3-20). A drop of the CH_4 concentrations and a concomitant increase of the CO_2 concentrations at that time indicates that CH_4 oxidation occurs deep into the soil near this well too. The $\delta^{13}C_{CH4}$ in microaerophilic soils exhibits strong seasonal variability with low $\delta^{13}C$ values in the summer and high values in the winter (Fig. 3-21). However, the $\delta^{13}C$ of methane in microaerophilic soil near well A10 follows a different trend. The $\delta^{13}C_{CH4}$ at probes installed at 2.0, 6.0 and 8.0 m from well A 10 decrease in winter (Fig. 3-22). The $\delta^{13}C$ compositions of C_2+ gases at the three sites vary less than the $\delta^{13}C$ of CH_4 with variability diminishing with increasing carbon numbers (Appendix 3).

The $\delta^{13}C$ composition of CO_2 exhibits the greatest isotope variability at well A10 (e.g., from -12 to -92 ‰; Fig. 3-23). However, average $\delta^{13}C_{CO2}$ of soil gas at this site (except for soils in the immediate vicinity of the well casing) remains close to -30 ‰ throughout the monitoring cycle. This along with the lack of vegetation on the site, indicates that oxidation of heavy oil is the most significant contributor of soil CO_2 (Fig. 3-23). In contrast, the variability of the $\delta^{13}C_{CO2}$ in soil gases collected from the microaerophilic and oxygen-rich soil at Edam reaches 15 ‰, with comparatively high values (e.g., -50 ‰) in summer and low (e.g., -70 ‰) in winter (Figures. 3-24 and 3-25). The $\delta^{13}C_{CO2}$ values at both Edam sites increase away from the wells.

Soil temperature

Soil temperature data is presented in Table 3-3 and Figure 3-26. The coldest months are February and March, whereas August is the warmest. The approximate annual average values estimated by linear interpolation of available data are similar (e.g., 7.3°C at 1.7 mbs and 8.0°C at 1.0 mbs, respectively). The temperature range at 1.7 mbs is smaller (i.e., 16°C) than that at 1.0 mbs (i.e., 19°C), though. At the Maidstone site soil temperature was measured from October 2003 until April 2004. For this time period differences in the temperatures between the Edam and Maidstone thermometers installed at 1.0 mbs ranged from +2.3°C in October to -1.4°C in March. The higher variability at Maidstone is likely caused by the complete lack of vegetation and the higher soil air permeability of the mixed gravel and sand cover that allows shallow soil to warm up and cool down faster. The deeper thermometer at Maidstone recorded a temperature that was about 1.0°C higher for most of the period but April 2004, when soil temperature was equal to that at Edam. Higher temperatures measured in the winter at this site are likely related to a better thermal insulation provided by the higher proportion of clay minerals in soil below 1.0 mbs (Chapter 2).

A limited number of soil temperature measurements is also available from microaerophilic soil at the two Edam sites in the fall/winter of 2003. The results are presented in Table 3-3 and on Fig. 25. Temperatures at well A3 in the fall were close to background soil temperatures. However, in mid October the former started to decrease more rapidly and in December the difference reached 3.4°C with the probe at 1.0 mbs recording a temperature as low as -3.9°C indicating a complete freezing of the shallow soil. In contrast, shallow soil temperatures at well A4 were similar to those measured at the background probes (Table 3-3). A comparison of the temperatures measured at 2.0 mbs at the two Edam sites shows that soils at A4 and at the background site had similar temperatures in late fall, although these were slightly lower at the A4 site in early fall. Soils temperatures at wells A3 and A10, however, were higher (by as much as 2.6°C) than the background soil temperatures for most of the time.

Discussion of Part II

Factors that control soil gas concentrations

A substantial increase of helium concentrations at the proximal probes at the two Edam sites coincides with a heavy rainfall (e.g., 65 to 75 mm) in west-central Saskatchewan on September 09, 2003 (Fig. 3-9). The increase is highest at well A4, and it is consistent with a reduction of soil air permeability that could result from the comparatively high soil moistures measured at this well at this time (cf. Moldrup *et al.*, 2001; Table 3-4). Thus, higher soil air permeability due to subsiding water table levels and low overall soil moisture contents in Western Canada, related to a period of drought throughout 2001 and 2002 (e.g., Wheaton *et al.*, 2005), appear to be the most likely explanations for the low He concentrations at the proximal probes in the summer and fall of 2003 (Fig. 3-9). A decrease in the He concentrations in the second half of the winter season is likely related to increasing soil air permeability through the frozen soil layer caused by coarsening of the ice crystals and ice/soil moisture sublimation facilitated by the constant flow of leaking gas.

The observed seasonal variability indicates that O_2 gas is consumed by aerobic bacteria during the oxidation of gaseous and liquid hydrocarbons. A contour map of oxygen concentrations shows that microaerophilic zone around well A3 extends laterally beyond 2.0 m (Fig. 3-11). In comparison, the microaerophilic zone at well A4 is significantly smaller (i.e., less than 1.0 m away from the well, not shown), while microaerophilic conditions prevail in probes installed as far as 6.0 m away from well A10 (not shown). High soil moisture and the related reduction of soil air permeability also have an impact on the O_2 content of microaerophilic soils. Low O_2 concentrations in soil gas samples collected immediately after soil thaws in the spring of 2003 probably reflect the combined effects of reduced soil air permeability and increasing microbial activity related to rising soil temperatures. Decreasing O_2 concentrations in soil gas samples collected after the heavy rainfall in September, 2003 at all monitoring sites are also likely to reflect reduction of soil air permeability and/or higher metabolic rates of the soil bacteria. Lower average O_2 concentrations at well A4, when compared to those at well A3, also coincide with generally higher soil moisture contents measured at this well (Table 3-4).

The heavy rainfall in September 2003 produced a lasting impact on soil methane concentrations (Fig. 3-13). While the CH_4 concentrations measured in the proximal probes at wells A3 and A10 decrease by as much as 30 %, a slight increase is observed at well A4 suggesting that the probe at A4 is installed closer to the leaking gas source. Methane concentrations in microaerophilic soils at Edam exhibit moderate variability throughout the monitoring period. Concentrations in the oxygen-rich soils in the summer are very low but increase by as much as four orders of magnitude in the winter (Figs. 3-14, 3-15). After the rainfall in September 2003, methane concentrations in the microaerophilic soil increased, while a decrease was observed in the oxygen-rich soils (Fig. 3-15). This decrease is consistent with temporary reduction of soil air permeability and, perhaps, higher rates of bacterial consumption in the oxygenated parts of the soil.

Biologically mediated processes in the soils

Methanotrophy

Rapidly decreasing methane and C_2+ gas concentrations away from the leaking gas sources, accompanied by a significant increase of the $\delta^{13}C_{CH4}$, virtual disappearance of O_2, and a significant increase of the concentrations of CO_2 of low to very low $\delta^{13}C$ (e.g., -30 to -90‰) indicate that that aerobic oxidation of gaseous and/or liquid hydrocarbons is the most significant biologically mediated process that occurs in soil near the three wells. The concentrations and stable isotope compositions of hydrocarbon gases and soil CO_2 also indicate that oxidation of methane is the dominant bacterially mediated process at the Edam sites, whereas oxidation of oil (and the by-products of oil degradation) dominates at the Maidstone site.

One of the goals of this chapter is to estimate the fraction of methane oxidized in the soils near the leaking wells. Rates for methane oxidation in soil are usually estimated by using stationary chambers to measure methane fluxes and attenuation in soil (Christofersen and Kjeldsen, 2000).

Although this is a viable technique when applied to landfills or wetlands where the methane flux is spread over large areas, it was not deemed a suitable approach in this study due to the inferred geometry of the gas plume in the soil. Observations of soil gas concentrations at the monitoring sites indicate that leaking gas enters the unsaturated zone from a confined source. This is supported by the examination of excavated well bores of leaking wells at Aberfeldy, Saskatchewan, which demonstrated that gas leakage is confined to a single annulus between the cement and the steel casing of the well. Therefore, the source of gas leakage could be regarded as a point source located at the intersection between the well bore and the capillary fringe.

The unsaturated zone comprises a three phase system that consist of a solid matrix, liquid, and gas. A fourth non-aqueous liquid phase is present in soils contaminated with liquid hydrocarbons. The distribution and behaviour of the mobile phases (e.g., water and gas) in soil is governed by their physical properties. Differences between the densities and viscosities of water and soil gas are approximately three orders of magnitude and, as a result, gas conductivities are significantly higher than hydraulic conductivities (Scanlon *et al.*, 2002). Gas flow velocities and flow directions in the unsaturated zone are not controlled by local ground water gradients (Bedient *et al.*, 1999). Instead, gas transport in soil occurs predominantly in response to pressure and concentration gradients (Mendoza *et al.*, 1995). Although the low dynamic viscosity of gases will results in a flow at very low pressure gradients, diffusion of gases in soil air is so rapid that some authors ignore advection as a transport mechanism (cf. Scanlon *et al.*, 2002). However, leaking gas transport in the unsaturated zone can not be driven by diffusion alone. High natural gas concentrations (ca. 100 % v/v) and very low CO_2 and O_2 concentrations measured in the proximal probes at the three monitoring sites suggest that leaking gas fluxes are large enough for advective transport to dominate in the soil near the wells. If concentration gradients were the sole driving force behind gas migration, CO_2 concentrations close to the well bores should have been high too. In addition, the depth of the Upper Cretaceous shales from where leaking gas originates is about 250 to 350 m (Rowe, 1998). Therefore, for gas to migrate outside the well casing, reservoir pressure must exceed the hydrostatic pressure at this depth. Thus, pressure gradient driven advection and buoyancy related to the low density of leaking gas should be the dominant factors that drive leaking gas transport in the unsaturated zone near the wells. The distance at which diffusion may become a dominant transport mechanism will depend on the flow rate and gas pressure and in the absence of flow rate measurements at the sites it is not possible to be determined.

Helium is a chemically inert gas that does not participate in biological processes. Thus, changes in He concentrations should reflect variations of natural gas flow rates, soil air permeability, and barometric pressure oscillations. Because of its conservative nature, helium has the potential to be an ideal tracer to help quantify bacterial oxidation of natural gas near the wells. Helium concentrations measured in the proximal probes at all three sites follow a similar trend suggesting that that gas leaking rates are constant and gas flow is at a steady state (Fig. 3-9). If steady state diffusion were the dominant gas transport mechanism, all gaseous species are expected to maintain constant volumetric ratios. The latter would allow the fraction of methane and C_2+ gases consumed by methanotrophic bacteria in the soil around the well to be estimated by applying the hydrocarbon gas/helium ratios. However, soil gas data from the monitored well sites show that the CH_4/He ratios at the proximal probes are consistently lower than the CH_4/He ratios at the rest of the probes in the microaerophilic zones (Fig. 3-27). Differences in the ratios between these sampling points amount to 50 % for CH_4 and even more for the C_2+ gases (not shown). If diffusion were the dominant form of gas transport, the ratio of helium to the hydrocarbon gases at steady state should have been lower away from the leaking gas source as there is plenty of evidence that hydrocarbon gases near the wells are consumed by bacteria. The same would have been true if the advective component were significantly higher than the diffusive component (cf. Ergas *et al.*, 2000).

Aerobic soil methanotrophs are particularly efficient in transforming the CH_4 carbon into cellular biomass and polysaccharide film (cf. Barker and Fritz, 1981, Borjesson *et al.*, 2001, Hilger *et al.*, 2000). The amount of carbon transferred to biomass depends on the growth efficiency, with more biomass produced at high growth rates and *vice versa* (Borjesson *et al.*, 2001). Therefore, the ratio of the concentrations of soil CH_4 and CO_2 assuming that all soil CO_2 is produced by methanotrophic bacteria, can be used to approximate the fraction of methane oxidized at different depths and distances from the well bore. This method could not be used at the Maidstone research site because of the isotope evidence for liquid hydrocarbon oxidation and other Terminal Electron Acceptor Processes (TEAP) such as methanogenesis that take place in the soil near the well head.

According to stoichiometric constraints, the amounts of CO_2 produced from the oxidation of 1.0 mole methane through the ribulose–monophosphate (i.e., Type I methanotrophs) and serine pathways (i.e., Type II methanotrophs) should be 0.52 and 0.59, respectively (cf. Hilger *et al.*, 1999). Much lower values (i.e., 0.12), however, are calculated for the former pathway by Gommers *et al.*, (1988). Those values are consistent with the results of incubation studies with soil samples from northern European landfill cover soils where values ranging from 0.09 to 0.38 are observed (Borjesson *et al.*, 2001). The results of Borjesson *et al.*, (2001) are likely to be more representative than those of pure culture experiments or experiments using specifically designed growth media where higher values are reported (cf. Templeton *et al.*, 2006). Therefore, for the purposes of this study a value of 0.2 was chosen.

For most probes except the ones installed at 1.0 m depth, close to the wells, the estimated amount of CH_4 oxidized approaches 100 %. The fraction of CH_4 oxidized at the probe installed at 1.0 mbs and 0.3 m distance (i.e., A1) from well A3 varies from less than 28 to more than 78 % with an average value of 60 % (Fig. 3-28). A significant decrease in the amount of CH_4 oxidized at well A3 seen in the fall of 2003 coincides with an apparent reduction in soil air permeability associated with higher soil moisture contents following the rainfall in September (Fig. 3-28). The average amount of CH_4 oxidized in soil at 1.0 mbs at well A4 is 20 % (Fig. 29). A significant increase of the amount of CH_4 oxidized in the winter coincides with higher $\delta^{13}C_{CH4}$ values measured at this probe (Appendix 3). Increasing methane consumption seems contradictory to the near freezing temperatures measured in soil at that depth. The most likely explanation is the inactivation of methanotrophic bacteria in the upper parts of the soil that allows for greater amounts of oxygen to reach deeper into the soil column, hence increasing the rates of CH_4 oxidation there. The inactivation is consistent with the observed increase of O_2 concentrations in deep soil at the sites at this time and it is the result of low soil temperature and/or moisture.

The variability of the estimated fraction of CH_4 oxidized in the microaerophilic soil near well A3 does not exhibit a simple seasonal relationship (Fig. 28). The pattern is less complicated at well A4 where CH_4 oxidation at 1.0 mbs increases in winter (Fig. 29). Oxygen and helium concentrations suggest that the observed increase of the estimated fraction of CH_4 oxidized is related to an apparent lack of O_2 consumption and an increase of soil air permeability in the upper soil. Thus, O_2 availability is the principal factor that controls CH_4 oxidation in these parts of the soil column at Edam. The higher CH_4 oxidation rates at 1.0 mbs in the winter (especially at well A4) show that the active zone of gas oxidation around the wells migrates downward.

Temperature variability has a distinct impact on the overall oxidation of leaking gas at the two Edam sites (Appendix 3). While at well A3 only about 0.1 % v/v of CH_4 escapes oxidation and reaches soil surface in the summer, sporadic measurements of high methane concentrations in the shallowest probes in the winter (see Appendix 3) indicate that the migration of the zone of active bacterial oxidation cannot compensate for the loss of methanotrophic activity in the upper parts of the soil profile. Therefore, between 30 and 80 % of the leaking methane is emitted to the atmosphere.

Kinetic isotope effect (KIE) of CH_4 oxidation at the monitoring sites

Two methods were used to estimate the values of the KIE associated with CH_4 oxidation in soil near the leaking wells. The first method uses the $\delta^{13}C$ of CH_4 and coexisting carbon dioxide assuming that soil CO_2 is produced solely by the bacterial oxidation of CH_4. The second method uses the initial $\delta^{13}C$ of CH_4 and the fraction of methane remaining (Coleman *et al.*, 1981). As discussed in Part I, the possibility of introduction of CO_2 from unrelated sources, such as the oxidation of biomass in field studies and also when bulk soil samples are used in laboratory incubations, limits the use of kinetic isotope fractionation factors estimated using the $\delta^{13}C$ of CH_4 and CO_2. To circumvent possible CO_2 contamination, most studies determine isotope fractionation by using the ratio of ^{13}C to ^{12}C in residual methane compared to that of unaltered methane. For closed systems the relationship between the isotope compositions of methane and the fraction of methane oxidized is expressed in the following equation (Coleman *et al.*, 1981; Borjesson *et al.*, 2001):

$$\delta^{13}C_m \approx \varepsilon \ln\left(\frac{F_m}{F_{ini}}\right) + \delta^{13}C_{ini} \qquad [3\text{-}5]$$

where $\delta^{13}C_m$ is the carbon isotope composition of residual CH_4 measured after the initiation of the experiment, $\delta^{13}C_{ini}$ is the initial carbon isotope composition, and F_m is the fraction of methane remaining. However, continuous supply of CH_4 and O_2 renders the soil near the leaking wells an isotopically open system. Thus, Rayleigh law need not apply (Barford *et al.*, 1999; Canfield, 2001) and the equation simplifies to:

$$\delta^{13}C_m \approx \varepsilon\left(\frac{F_m}{F_{ini}}\right) + \delta^{13}C_{ini} \qquad [3\text{-}6]$$

The value of ε is the slope of a regression line defined by plotting the initial ($\delta^{13}C_{ini}$) and measured methane ($\delta^{13}C_m$) compositions at different depths and distances near the Edam wells vs. the estimated fraction of methane remaining. Initial carbon isotope compositions of methane ($\delta^{13}C_{ini}$) are approximated by the average $\delta^{13}C$ of gases collected from the proximal probes having total hydrocarbon concentrations above 85 % v/v (Table 3-5).

$\varepsilon_{CH4-CO2}$ values

Estimated $\varepsilon_{CH4-CO2}$ values are different not only at the three wells but also in different parts of soil around the wells (Figures 3-30, 3-31, 3-33). The apparent $\varepsilon_{CH4-CO2}$ values at the sites vary from -41 to +48. Negative values at Edam are estimated from samples collected from the proximal probes and occasionally from the probes placed at 1.0 mbs and 0.3 m distance from the well bore (well A3). At well A4 negative values are also estimated for samples collected from almost all probes installed >1.0 m away from the well or in oxygen-rich soil (Fig. 3-31). Positive values at this well are estimated only from the samples collected from the single probe installed in microaerophilic soil (i.e., A11). A few very low and even negative values (i.e., as low as -8 ‰) are also estimated from samples collected from A11 in the summers of 2002 and 2003. Negative values at Maidstone are estimated from samples collected from all probes, while positive values are only estimated for some samples collected from shallow soil (i.e., 0.2 mbs and 0.3 m distance from the well).

With the exception of the proximal probes, the $\varepsilon_{CH4-CO2}$ values at the two Edam sites exhibit clear seasonal variability with high values in the winter and low values in the summer (Figures 3-30, 3-31). The largest $\varepsilon_{CH4-CO2}$ at well A3 are estimated from samples collected at probe A2 in the winter, whereas the smallest (and occasionally negative fractionations) are estimated from samples collected at probe A1. Differences between the $\varepsilon_{CH4-CO2}$ values estimated at these two probes are smaller in the summer and larger in the winter (Fig. 3-30).

Apparent $\varepsilon_{CH4-CO2}$ values from the different probes at well A3 also correlate with temperature (Fig. 3-32), although no statistically significant correlation exists at wells A4 and A10. Correlation between temperature and isotope fractionation was observed in laboratory incubation studies but was never measured on the field before (Coleman *et al.*, 1981; Tyler *et al.*, 1994; Chanton and Liptay, 2000; Borjesson *et al.*, 2001). With the exception of the study of Coleman *et al.* (1981), correlations between these two variables are negative with fractionations that vary from 0.2 to 0.5 ‰ per degree

Celsius. The values estimated in this study, however, are much higher and for samples collected at probes A1 and A2 are 0.9 and 1.3 $\varepsilon_{CH4-CO2}$/°C, respectively.

$\varepsilon_{CH4m-CH4ini}$ values

Estimated $\varepsilon_{CH4m-CH4ini}$ values at wells A3 and A4 vary from 11 to 32 (Figs. 3-34 and 3-35)[6]. The two figures 3-34 and 3-35 show that the $\varepsilon_{CH4m-CH4ini}$ values exhibit the same general trend like the $\varepsilon_{CH4-CO2}$ values with low values in the summer and high values in the winter. While there is a pretty good overlap between the $\varepsilon_{CH4m-CH4ini}$ and the $\varepsilon_{CH4-CO2}$ values at well A3 in the 2001/2002 and 2002/2003 winters the estimated values diverge by more than 10 ‰ in the summer of 2003 and in the winter of 2003/2004 (Fig. 3-34). In contrast, estimated $\varepsilon_{CH4m-CH4ini}$ values at well A4 are on average 10 ‰ higher than the $\varepsilon_{CH4-CO2}$ through the entire monitoring period.

A comparison between the $\varepsilon_{CH4m-CH4ini}$ values at wells A3 and A4 demonstrates that fractionations at the two wells follow the same general trend. However, one significantly lower value (i.e., up to 9 ‰) is estimated at well A4 in the beginning of the winter of 2002/2003 (Fig. 3-35).

Factors that control carbon isotope fractionation factors

Kinetic isotope fractionation values estimated from soil gas samples collected near the two leaking wells at Edam span the entire spectrum of reported isotope fractionations in the literature (cf. Whiticar, 1999). The observed seasonal variability and correlation with soil temperature indicates that the temperature is the single most important environmental parameter that controls the estimated isotope fractionation values. Negative correlation between temperature and isotope fractionation is common for a broad range of inorganic reactions between phases that are in thermodynamic and isotope equilibrium. In living systems however, isotope fractionation results from irreversible kinetic reactions that may or may not proceed to completion (cf. Hayes 2001). Although the impacts of temperature on KIE were determined from incubation studies in the past (e.g., Coleman *et al.*, 1981; Borjesson *et al.*, 2001, Jahnke *et al.* 1999, amongst others), little explanation was provided about the mechanisms responsible for the observed temperature variability.

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[6] The $\varepsilon_{CH4m-CH4ini}$ and $\varepsilon_{CH4-CO2}$ values on figure 3-34 comprise averages of the respective values estimated from probes installed in microaerophilic soil, whereas figure 3-35 shows $\varepsilon_{CH4m-CH4ini}$ and $\varepsilon_{CH4-CO2}$ values estimated from the only probe installed in microaerophilic soil at this site (i.e., A11).

Correlation between KIE and parameters other than temperature was reported for plants as well as for unicellular organisms. For example, early studies established that nitrogen isotope fractionation related to plant uptake of NO_3^- mediated by the Nitrate Reductase enzyme approaches zero when substrate is limiting and has a maximum value where the substrate is abundant (Mariotti *et al.*, 1982). These authors, therefore, assumed that the isotope effect is the sum of isotope effects related to nitrate uptake by the plant and the enzymatic fractionation. Because the NO_3^- uptake has no isotope effect, there will be no fractionation when enzymatic activity is high (i.e., high growth rates) and the uptake rate is limiting and *vice versa*. Later studies on the uptake of NH_4^+ by heterotrophic bacteria demonstrate that lower nitrogen stable isotope fractionation at low (micro molar) NH_4^+ concentrations is related to a switch from the Glutamate Dehydrogenaze enzyme, that exhibits higher isotope discrimination, to the Glutamine Synthase enzyme (Hoch *et al.*, 1992). These authors also attributed observed isotope fractionation variation in part to the cellular transport mechanisms employed by the microorganisms and concluded that the transport mechanism is unlikely to have a significant impact on ε as long as isotope equilibrium is established between the substrate outside and inside the cells (Hoch *et al.*, 1992).

Direct relationship between KIE, growth rate, and substrate availability was also observed in photosynthesizing marine algae (cf. Popp *et al.*, 1998; cf. Freeman, 2001). Experiments with different algae demonstrated that when substrate ($CO_{2(aq.)}$) is abundant, carbon isotope fractionation is high and *vice versa* (Popp *et al.*, 1998). These authors concluded that at zero growth rates and abundant substrate observed maximum isotope fractionation is this of the Rubisco enzyme, although they were unable to provide an explanation about the observed growth rate related variability (Popp *et al.*, 1998; cf. Freeman, 2001). Popp *et al.* (1998) also pointed out that both the size and geometry of the cells exhibit positive correlation with isotope fractionation, which implies the existence of intracellular transport related isotope discrimination.

In their incubation experiments Summons *et al.* (1994) and Jahnke *et al.* (1999) observed high $\varepsilon_{CH4-biomass}$ (e.g., 31 ‰) during the stage of exponential growth that diminished by a factor of 2 during the stationary phase. Incubation experiments with Type I methanotrophs demonstrated that if microorganisms used the particulate form of the methane monooxy[illegible]ze enzyme (pMMO), fractionations were two times higher than if the soluble form of MMO (sMMO) were used (Jahnke *et al.*, 1999). Summons *et al.* (1994) and Jahnke *et al.* (1999) also established that substrate (CH_4(aq.)) limitation has a significant impact on the magnitude of isotope separation. The limiting role of methane concentration was also evident from the study of Tyler *et al.* (1994), who observed that metabolic reactions related to the oxidation of atmospheric levels of methane (i.e., 1.7 ppmv) exhibit very low isotope discrimination (e.g., 3 ‰). Although overall fractionation determined by Tyler *et al.* (1994) is 22 ‰, the authors attribute the remaining 19 ‰ to kinetic effects related to gaseous diffusion. Teh *et. al.* (2005) also observed that at CH_4 concentrations greater than 1,400 ppmv estimated fractionation is 25 ‰, whereas at concentrations below 1,400 ppmv isotope fractionation falls to 12 ‰.

In a set of incubation experiments with Type I and II methanotrophs Templeton *et al.* (2006) also observed larger $\varepsilon_{CH4-biomass}$ in the beginning of their experiments. In contrast to the results of Summons *et al.*, (1994) Jahnke *et al.* (1999), however, Templeton *et al.* (2006) did not observe MMO-type related fractionation. Instead, they observed a correlation between KIE and the amount of methane oxidized per unit time that strongly correlates with cellular density. The highest and lowest $\varepsilon_{CH4-CO2}$ observed in the experiments of Templeton *et al.*, (2006) at low and high cellular densities are 35 and 3 ‰, respectively. Therefore, those authors assumed that the former is the maximum ε value mediated by the MMO enzyme. Based on their results Templeton *et al.* (2006) assumed that when cellular densities (and thus the amount of MMO) increase, the first step (i.e., the aqueous diffusion of

CH_4) becomes limiting and, as a result, isotope fractionation approaches this related to aqueous diffusion of methane alone. In other words, when the ratio of $CH_{4(aq.)}$ to MMO (cellular density) in the milieu is high fractionation is large and *vice versa*. However, if cellular density alone controls isotope fractionation, the low isotope fractionations observed at the Edam research sites would imply that significantly lower amounts of methane are oxidized in the winter. Although cellular densities were not measured in this study, estimated amounts of methane oxidized in particular portions of the soil near the leaking wells (i.e., probes A1 and A11) did not decrease as those measured in the early phases of Templeton *et al.* (2006)'s experiments, when comparable high KIE values were observed. Therefore, factors other than cellular density must have an impact on the isotope fractionation in soil near the wells.

The Q_{10}[7] values determined for methanotrophic bacteria vary from 1.4 to 2.1 providing direct evidence for the importance of temperature in the metabolism of methanotrophic bacteria (Hanson and Hanson, 1996). Temperature is an important regulator of enzyme activity (cf. Huston *et al.*, 2000) and studies of extracted pMMO show a significant drop in enzymatic activity with temperature (Takeguchi *et al.*, 1998). Consequently, as a result of decreasing enzyme activity diffusion of methane through soil water will cease to be a rate limiting step and isotope fractionation will increase. Therefore, temperature related decrease in MMO activity will have the same effect on isotope fractionation as reducing cellular density.

Difference between $\varepsilon_{CH_4ox-CH_4ini}$ and $\varepsilon_{CH_4-CO_2}$

As mentioned earlier, estimated $\varepsilon_{CH_4ox-CH_4ini}$ values at well A3 are on average 10 ‰ higher that the $\varepsilon_{CH_4-CO_2}$ in winter (Fig. 3-34), while the same difference appears to exists at well A4 through the entire year. Reservoir effects related to the accumulation of CO_2 in microaerophilic soil should result in higher $\varepsilon_{CH_4-CO_2}$ values and, thus, cannot explain the observed differences. The study of Templeton *et*

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[7] Q_{10} is the factor by which physiological processes and biochemical reactions increase when temperature increases with 10 degrees °C.

al. (2006) demonstrates that cellular biomass exhibits constant ^{13}C enrichment when compared to co-produced carbon dioxide. For Type I methanotrophs this enrichment is 16 ‰ while for Type II methanotrophs it is only 6 ‰ (Templeton *et al.*, 2006). The smaller enrichment at Type II methanotrophs is due to the incorporation of CO_2 into biomass during the serine pathway for carbon assimilation (Hanson and Hanson, 1996). Type II methanotrophs incorporate 30 to 50 % of their cellular carbon from CO_2 that in most cases is the direct product of the oxidation of methane. Thus, mass balance requires that at steady state apparent $\varepsilon_{CH4-CO2}$ should always have a higher value than $\varepsilon_{CH4m-CH4m}$. Even if significantly larger amount (i.e., >80 %) of CH_4 carbon is transferred to CO_2 instead of to biomass, the $\varepsilon_{CH4m-CH4m}$ values can never be smaller than the $\varepsilon_{CH4-CO2}$ values. Indeed the $\varepsilon_{CH4-CO2}$ values estimated from the data of Templeton (2006) are consistently larger than their $\varepsilon_{CH4m-CH4m}$ values. Because MMO fractionates the isotopes independently of the carbon assimilation pathway, the cellular biomass of Type II methanotrophs will contain a smaller proportion of ^{13}C enriched CH_4 carbon. Thus, differences between $\varepsilon_{CH4m-CH4m}$ and $\varepsilon_{CH4-CO2}$ values for Type II bacteria will be smaller than those for Type I bacteria.

As discussed, "negative" $\varepsilon_{CH4-CO2}$ values indicate the introduction of CO_2 from a source unrelated to methanotrophy (i.e., carbon dioxide derived from the oxidation of liquid hydrocarbons, methanogenesis via acetoclastic fermentation or modification of the $\delta^{13}C$ compositions of residual CO_2 by methanogenesis via carbonate reduction. Acetoclastic fermentation of by-products of oil degradation may also contribute methane of low $\delta^{13}C$ that will shift $\varepsilon_{CH4-CO2}$ further into negative territory. While the lack of methanotrophy at the proximal probes is evident from the low $\delta^{13}C$ values of methane and the small amounts of CO_2 of high $\delta^{13}C$, negative $\varepsilon_{CH4-CO2}$ values at Maidstone are estimated from samples that contain methane of comparatively high $\delta^{13}C$ and that also contain significant amounts of carbon dioxide. Thus, despite evidence for methanotrophy in the soil near this well, the amount of CO_2 produced from the microbial oxidation of methane is small compared to the amount of CO_2 produced from the direct oxidation of heavy oil and/or from the fermentation of by-products of oil degradation. Lack of vegetation at this site precludes the presence of significant quantities of soil respired CO_2 (Chapter 2). Therefore, the difference between the observed $\varepsilon_{CH4m-CH4in}$ and $\varepsilon_{CH4-CO2}$ values and the very low, and especially the negative $\varepsilon_{CH4-CO2}$ values, are inconsistent with methanotrophy being the principal microbially mediated process, and suggest that the $\delta^{13}C$ compositions of CO_2 and/or CH_4 near the Edam wells have been modified by other processes. Such processes include aerobic and/or anaerobic oxidation of SOM and liquid hydrocarbons that would produce soil CO_2 of similar and often indistinguishable carbon isotope compositions (e.g., -22 to -30 ‰; Chapter 6). Another process that can modify the isotope composition of both CH_4 and CO_2 is methanogenesis.

Aerobic oxidation of C_2+ gases

The $C_1/\Sigma C_2$+ ratios of gas samples collected in microaerophilic soils near the wells in summer are lower than the "primary" ratios measured in the proximal probes. The same relationship is observed in the summer subgroup of samples from Group III soil gases (Part I, University of Alberta gas database). This suggests that CH_4 is preferentially oxidized in summer. Similarly to what was observed in samples from the University of Alberta data base, the $C_1/\Sigma C_2$+ ratios of soil gas samples from the monitoring sites at Edam increase significantly in winter. The possibility that this increase is caused by the addition of CH_4 of bacteriogenic origin was rejected in Part I due to the intolerance of methanogenic archaea to low temperatures. It was hypothesized instead that increasing ratios reflect: a) predominant oxidation of C_2+ gases; b) slowing down the CH_4 oxidation rate but not the rates of C_2+ gas oxidation; c) differences in the physical properties of the n-alkane gases. Although a slight decrease of the $\delta^{13}C$ values of C_2+ gases is observed in winter, the variability is rather non-systematic. Attempts to correlate C_2+ isotope compositions with temperature (not shown) did not produce statistically significant results either. Therefore, the $\delta^{13}C$ compositions of C_2+ gases are not consistent with preferential oxidation of these in winter. Aerobic oxidation rates of some n-alkanes (e.g., ethane, propane) by methanotrophic bacteria in culturing assays are comparable to those of CH_4, and slower rates have been estimated for more complex hydrocarbons (cf. Higgins *et al.*, 1981). Rates of CH_4 to n-C_4H_{10} oxidation in microcosm experiments simulating marine estuarine systems, however, increase with increasing chain length (Bopp *et al.*, 1981). In addition, both the oxidation rates and the differences between the oxidation rates of different n-alkanes observed decrease at lower temperatures (Bopp *et al.*, 1981).

Preferential oxidation of C_2+ gases is observed in natural gas reservoirs (James and Burns, 1984; Cai et al,. 2002; Martini *et al.*, 2003). The process is characterized by the bacterial consumption of propane and/or ethane that results in ^{13}C-enrichment of both gases. The $\delta^{13}C$ of CH_4, however, is not modified and it is thus presumed that methane is not consumed but may even be produced (Dimitracopoulus and Muehlenbachs, 1987; Martini *et al.*, 2003). The presence of reduced sulphur species in the gas reservoirs indicates that the preferential oxidation of C_2+ gases is an anaerobic process. It is also suggested that the latter is mediated by a consortium of methanogens and sulphate reducing bacteria similar to this that operates in marine environment (Martini *et al.*, 2003).

To determine if there were preferential oxidation amongst the C_2+ gases in soil gas samples collected at the monitoring sites, the molecular ratios and stable isotope separations of ethane to propane and iso-butane to normal butane (e.g., $\Delta_{propane-ethane}$; $\Delta_{i-butane-n-butane}$) are compared to those of gas samples collected from the proximal probes (Figs. 3-36a, b; 3-37a, b). If there were selective bacterial oxidation of one particular component with respect to another, both the ratios and isotope separations should have changed. Results show that there is a significant seasonal variability of the molecular ratios in shallow soil with values lower or identical to those of the "initial" gas in the summer and higher in the winter (Figs. 3-36a; 3-37a). Although the higher C_2/C_3 ratios appear to be consistent with preferential oxidation of propane, the $\delta^{13}C_{propane}$ and the $\Delta_{propane-ethane}$ of these gases do not change significantly. Only in one probe, installed at 0.3 m distance and 1.0 mbs from well A3, did there appear to be a concomitant change of C_3/C_2 and $\Delta_{propane-ethane}$ suggesting that preferential oxidation of propane occurs (Fig. 3-36a, b). Similar relationship is not observed at the other probes and well sites, however. Therefore, changes in the C_2+ molecular ratios in winter are related to differences in their physical properties. This is corroborated by the extreme changes in C_2+ gas concentrations observed in the upper parts of the soil that freezes in winter, whereas significantly smaller changes or lack of thereof are observed in the deeper soil horizons where temperatures are above freezing (Fig. 3-36a).

Methanogenesis

The δ^{13}C of methane in shallow (e.g., 1.0 mbs) microaerophilic soil, very close to well A3, increases significantly in the summer and then in spite of the significant reduction of the estimated fraction of methane remaining, changes little or does not change at all in the microaerophilic soil further away from the well (Fig. 3-21). In some instances, $\delta^{13}C_{CH4}$ values of samples for which higher amounts of oxidized methane are estimated are lower than the $\delta^{13}C_{CH4}$ of samples that demonstrate lesser oxidation. According to this observation, it appears that methanotrophic bacteria away from the well consume indiscriminately the $^{13}CH_4$ and $^{12}CH_4$ molecules. This could be seen when the $\delta^{13}C_{CH4}$ are plotted against the fraction of methane remaining. The plotted values exhibit deviation from a straight line towards a line having a shallower slope at low concentrations is prominent in the summer (Fig. 3-37c). This deviation can not be explained by processes related to CH_4 oxidation but it is rather consistent with addition of methane of low δ^{13}C.

It could be seen on Fig. 3-38a that the addition of 5 % v/v of CH_4 having δ^{13}C of -55 ‰, that would be the δ^{13}C composition of CH_4 produced from fermentation of OM with δ^{13}C of ca. -35 ‰ found in soil at the well sites (Chapter 5), would result in changes in δ^{13}C values and concentrations similar to those observed in the summer months at well A3 (Fig. 3-38c). If the δ^{13}C [illegible] methane is -70 ‰, that would be consistent with methanogenesis via carbonate reduction, then adding 5 % v/v of methane produces a much more distinct deviation from a straight line (Fig. 3-38b). Such low amounts of CH_4 (i.e., 5-10 %) are close to or within the estimated analytical error of the analytical method used, and are thus difficult to account for. However, probes in the microaerophilic soil at well A3 exhibit elevated CH_4 contents and higher CH_4/He ratios in the summer. Although this increase may in part be the result of depressed oxidation rates due to O_2 over consumption by methanotrophic bacteria, the presence of low $\delta^{13}C_{CH4}$, deduced from the deviation observed on the graphs, still requires continuous addition of bacteriogenic methane. Addition of bacteriogenic methane is evident at well A10 where the $\delta^{13}C$ of CH_4 collected in a probe installed as far as 8.0 m from the well casing has lower $\delta^{13}C$ than the $\delta^{13}C$ of the "initial" gas at the site (Appendix 3).

The $\delta^{13}C$ of CO_2 also reflects presence of CO_2 not related to bacterial oxidation of CH_4 in soil near the three wells. A 10 ‰ difference between estimated $\varepsilon_{CH4-CO2}$ and $\varepsilon_{CH4m-CH4m}$ at well A3 in the summer and the very low and/or positive $\varepsilon_{CH4-CO2}$ at well A4 suggest that high $\delta^{13}C$ carbon dioxide is added to the soil gas. A gas sample collected from shallow soil near well A3 in July 2001 contains CO_2 with a $\delta^{13}C$ value of -29 ‰ (Appendix 3). CO_2 of similar, high $\delta^{13}C$ (e.g., -22 ‰) was also collected from microaerophilic soil at the same well, at the beginning of the monitoring cycle. High $\delta^{13}C$ values were recorded through the first month in shallow soil, and for up to several months into the deep soil (Appendix 3). As discussed, possible sources of CO_2, other than methanotrophy, are aerobic oxidation of soil organic matter, presence of "primary" CO_2 that originates in the subsurface and is a part of the leaking gas, or CO_2 generated by fermentation and methanogenesis.

The very low amounts of CO_2 and/or low $\delta^{13}C_{CO2}$ measured in soil gas samples collected at the proximal probes indicate that advective flux of leaking gas prevents soil respired CO_2 from reaching parts of the soil close to the source of leaking gas. Low O_2 contents in microaerophilic soil would also suppress the metabolism of heterotrophic bacteria. In addition, the isotope effect of mixing CO_2 produced from the oxidation of methane with background CO_2 in microaerophilic soils near the Edam wells is estimated to be less than 1.0 ‰. Therefore, heterotrophic bacterial metabolism is unlikely to contribute significant (if any) CO_2 in soil near the wells.

The average amount of CO_2 measured at the proximal probe at well A3 is 3000 ppmv, and it is about one order of magnitude less (i.e., 370 ppmv) at well A4. If "primary" CO_2 of high $\delta^{13}C$ (e.g., -10 to -20 ‰) mixes with CO_2 of low $\delta^{13}C$, produced from the bacterial oxidation of methane, a positive correlation between the amount and $\delta^{13}C$ of CO_2 should be evident. No such relationship is seen at the two Edam wells, however, suggesting that there is no flux of "primary" carbon dioxide of high $\delta^{13}C$ at both sites. Lack of correlation also indicates that variable $\delta^{13}C$ compositions of soil CO_2 near the leaking gas sources do not result from mixing with such gas(es) but rather reflect mixing between high and low $\delta^{13}C_{CO2}$ produced *in situ*. There appears to be no influx of "primary" CO_2 at well A10 either, where very low CO_2 concentrations (e.g., 61 ppmv) with a $\delta^{13}C$ as low as -67 ‰ are measured in samples from the proximal probe. Therefore, methanogenesis is the most likely contributor of "high" $\delta^{13}C$ CO_2 in the microaerophilic soil at all three wells.

Evidence of anaerobic conditions in soil near the leaking wells

Although some methanogenic archaea operate in microaerophilic conditions (Kumaraswamy *et al.*, 2001), methane production occurs in strictly anaerobic conditions (Oremland *et al.*, 1988). High natural gas concentrations and negligible amounts of O_2 and CO_2 in samples collected close to the sources of leaking gas are consistent with advective natural gas transport from the well. Establishment and maintenance of anoxic conditions is facilitated by the slow diffusion of O_2 in soil water. Anaerobic conditions in soils are not unusual. Anaerobiosis is prevalent under high water saturation and/or is maintained by bacterial consumption of O_2 during the mineralization of a variety of carbon sources. However, soil at 0.5 mbs at Edam contains ca. 5 % water (Table 3-4). Such low soil moisture contents cannot fill in the pores of the sandy soils at the sites and moisture is thus unlikely to have any role in reducing O_2 concentrations. Instead, what renders soil domains near the wells anaerobic is the rapid consumption of oxygen related to the high rates of aerobic oxidation of CH_4.

It is worth noting that in the summer O_2 concentrations in shallow soil close to wells A3 and A4 are lower than those measured in the proximal probes (Appendix 3). Therefore, in addition to mechanical displacement (i.e., by advective flux of leaking natural gas), bacterially mediated oxidation of natural gas and oil also plays an important role in maintaining O_2 levels in the microaerophilic soils low (cf. Lahvis and Baehr, 1996). Due to low aqueous solubility of O_2, soil air oxygen concentrations of less that 2.0 % v/v would translate into less than 1.0 mg/l of dissolved oxygen in soil water, at the range of soil temperatures measured at the sites. Similar and even higher amounts of dissolved O_2 are tolerated well by facultative anaerobic bacteria (Imhof and Heinzer, 1996; Costa *et al.*, 2000). Therefore, conditions favourable for anaerobic bacteria exist near the leaking wells.

The presence of authigenic pyrite and/or siderite in the soil around the wells also corroborates the hypothesis that anaerobic conditions are common is these parts of the soil (Chapter 4). For pyrite to be stable, soil Eh of the medium must be between -200 and -350 mV, which requires virtual absence of dissolved and/or gaseous O_2. Authigenic siderite also precipitates in strictly anaerobic environments (Romanek *et al.*, 2003; Ohmoto and Watanabe, 2003). The dark grey to green color of soils near the wells, especially in the deeper soil horizons, is another evidence of O_2 deficiency. Dark soil colors indicate the predominance of Fe^{2+} minerals, such as magnetite and green rust $[Fe^{2+}_4\ Fe^{3+}_2\ (OH)_{12}]^{2+}\ [CO_3\ 2H_2O]^{2-}$, the latter being stable only in the absence of oxygen (Williams and Scherer, 2000). A closer look at the SEM image of the pyrite framboid from shallow soil at well A3 shows evidence of dissolution and reprecipitation (Chapter 4). Some grains have cubic voids in their central portions indicative of partial dissolution and/or replacement of pyrite by some other Fe (?) bearing phase, likely iron hydroxide (goethite) or sulphate (jarosite). The presence of those textures is thus consistent with transient conditions where oxygen content is low to nonexistent at high O_2 (and CH_4) consumption rates and/or soil moisture and *vice versa*.

Indirect evidence for prevalent anoxic conditions, especially in the deep parts of the soils around the leaking wells, are also the measured high soil pH values (see Chapter 6). Studies of methanogenic environments demonstrate that neutral or elevated pH conditions exist in sediments and slurries where methanogenic rates are high (Mormile *et al.*, 1996; Segers, 1998). Dissections of termites also demonstrate that CH_4 is produced in the posterior guts of the insects where pH as high as 11 is measured (Schmidt-Wagner and Brune, 1999). Elevated soil pH near some wells may also be explained by contamination with soda ash (e.g., Na_2CO_3), a common drilling-fluid additive or by bacterial processes following nitrogen fertilization. Soda ash, however, has high water solubility and rapidly dissociates to Na^+ and CO_3^{2-}. Thus, elevated soil pH in soil samples collected as far as 8.0 m away from well A10, or in soils near older wells, can not be consistent with soda ash contamination. In addition, if high soil pH were related to agricultural activities, then nearby background soils should also have high pH. Background samples however, do not exhibit elevated pH.

Methanogenic substrates

Fermenting and acetogenic microorganisms degrade organic matter to acetate and hydrogen via a complex set of reactions. Acetate is formed by the fermentation of hydrolysed organic matter whereas hydrogen is produced by acetogenic bacteria that convert complex organic substrates (EPS, and etc.) into H_2 and fatty acids (Chapelle *et al.*, 2002). Lovely and Godwin (1988) demonstrate that dissolved hydrogen concentrations depend on the types of terminal electron acceptor processes that dominate in anaerobic sediments and aquifers. The concentrations of dissolved hydrogen are less than 0.05 nM for sediments where nitrate reduction takes place, 0.2 for Fe^3+ reduction, 1 to 1.5 nM for sulphate reduction and 7-10 nM for methanogenesis. Methanogenic reactions may proceed at higher H_2 concentrations, if local pH and/or the amounts of substrate utilized (e.g., alcohols and/or fatty acids) are high (Conrad *et al.*, 1985). By keeping H_2 partial pressure low, H_2-consuming microorganisms render biological processes such as fermentation of ethanol, propionate, and other fatty acids thermodynamically feasible. Fermentative bacteria are protected from high H_2 concentrations by sharing microenvironments with the H_2 consuming methanogens (Conrad *et al.*, 1995). Hydrogen consuming methanogens also alter the metabolism of fermentative bacteria so that the latter may produce significantly more oxidized compounds (Conrad *et al.*, 1985).

Although there are no measurements of the acetate content of soil water near the wells, H_2 concentrations are measured in most soil gas samples. H_2 concentrations in soil gas in the microaerophilic zone near well A3 at Edam vary from 0.8 to 40.2 ppmv (i.e., 0.8 to 38 nM of dissolved hydrogen) with an average value of 7.4 nM (one high concentration of 103 ppmv measured in August, 2003 was excluded from the data set during the statistical treatment). Similar concentrations of dissolved hydrogen are estimated in one microaerophilic probe at well A4 and in the proximal probe at well A10 at Maidstone. Estimated dissolved hydrogen levels in the soil pore water at these sites are, therefore, consistent with bacterial methanogenesis according to the criteria of Lovely and Goodwin (1988).

Hydrogen concentrations in shallow microaerophilic soil near the Edam wells are measurable only in the summer indicating intermittent hydrogen production consistent with intermittent methanogenesis. The relatively constant, one order of magnitude higher H_2 concentrations measured at well A4, compared to those at well A3, throughout the entire year, indicate the presence of a stronger hydrogen producing bacterial community. Despite the high H_2 concentrations that may inhibit the activity of some acetoclastic methanogens, (i.e., Mormile *et al.*, 1996), the consistently low $\varepsilon_{CH_4-CO_2}$ values as compared to the $\varepsilon_{CH_{4m}-CH_{4ini}}$ (by ca. 10 ‰) suggest that methanogens are active at this well site (cf. Magot *et al.*, 2000).

Microbial biomass, exopolysaccharide film, and residual SOM are the most likely substrates available to fermentative bacteria in the soils near the Edam wells. SEM imaging reveals that abundant polysaccharide production at Edam is associated with bacterial communities that precipitate calcite (Chapter 4). Methanotrophic bacteria are also known to produce series of intermediates, such as methanol and formaldehyde (Costa *et al.*, 2000). Acetate production has also been observed in cultures of methanotrophic bacteria under O_2 limiting conditions (Costa *et al.*, 2000). In addition, methanotrophs may also produce proteins (cf. Costa *et al.*, 2000). All of the compounds listed above can be used by the methanogenic consortium.

Extensive liquid hydrocarbon contamination, elevated H_2 concentrations, and high $\delta^{13}C$ of soil CO_2 are evidence of the existence of a methanogenic consortium in the microaerophilic soil at well A10. Liquid hydrocarbons are partially oxidized by both bacterially mediated and inorganic reactions (Hunt, 1979; Cozzarelli *et al.*, 1994). The oxidation of parafinic compounds produces low molecular weight alcohols, aliphatic acids, esters (acetate), and ketones (Dimitrakopoulos and Muehlenbachs, 1987). Oxidation also cleaves the bridge structures binding the aromatic compounds and produces water-soluble organics (e.g., phenols, aldehydes, ketones, and various carboxy-, hydroxy- and methoxy- bearing compounds), nitrogen-bearing compounds (pyridines and amines), mono- and polycyclic aromatic hydrocarbons (PAH's), and to a lesser degree, aliphatic compounds. Most of these compounds would be fertile substrates for fermentative bacteria growth in soil near wells contaminated by liquid hydrocarbons.

Soil temperature and methanogenesis

Both the lack of H_2 in shallow soil at the A3 Edam site, and the very high H_2 concentrations at well A10 suggest a disruption in methanogenic archaeal metabolism in the winter. Methanogens have relatively slow growth rates and are more sensitive to environmental changes than fermentative bacteria (cf. Mormille *et al.*, 1996). As a result, a number of environmental variables may suppress or inhibit methanogenesis. These include carbon starvation caused by competition with aerobic microorganisms and competitive terminal electron processes involving SO_4^{2-}, Fe^{3+} and NO_3^-. Although the mechanism of suppression is not clear, it is known that the free energy (ΔG) supplied by anaerobic oxidation of labile organic matter or other carbon-bearing substrates is higher than the ΔG supplied by methanogenesis. Formation of toxic intermediates during denitrification and sulphate reduction also inhibits methanogenesis (Jackel and Schnell, 2000; Segers, 1998). Incubation experiments involving pure cultures and bulk soil/sediment samples reveal that methanogenic bacteria have high average Q_{10} values and are, therefore, highly sensitive to temperature changes (Segers, 1998). The observed seasonal variability of H_2 soil gas concentrations therefore, indicates that soil temperature and/or oxygen availability are the most likely suppressors of methanogenesis at some monitoring sites. While soil freezing at Edam appears to effectively halt the metabolism of all three communities from the methanogenic consortium, the four order of magnitude increase of H_2 concentrations at well A10, that coincides with low CH_4 and O_2 soil gas concentrations, suggests a decoupling in the methanogenic consortium. Similar high H_2 concentrations are observed in sediments and sewage sludge where there is a high input of organic matter disrupting steady state conditions (Lovely and Goodwin, 1988; Mormile *et al.*, 1996). Even higher H_2 concentrations are found in landfill soils and in soil contaminated with liquid hydrocarbons (Mormile *et al.*, 1996; Lundergard *et al.*, 2000). The landfill soils also contain high concentrations of volatile fatty acids and have low counts of methanogenic archaea. As mentioned, high H_2 concentrations (e.g., >2.0 μM) are known to depress pH and to inhibit methanogenesis mediated by some acetoclastic methanogenic archaea (Mormile *et al.*, 1996). Excess H_2 disturbs the flow of electrons and prevents acetate fermentation (Zinder and Anguish, 1992). Accumulation of fatty acids that result from reduced acetogenic activity may bring the pH of the milieu down. The latter along with falling temperatures disrupts methanogenesis and results in low hydrogen uptake and the accumulation of H_2 and organic acids (Lovely and Klug, 1982).

Other TEAP's in soil near the leaking wells

Elevated soil pH (and alkalinity) may also be associated with other anaerobic terminal electron processes, such as denitrification, ammonification of urea, and SO_4^{2-} related anaerobic oxidation of organic matter and methane. The significantly lower concentrations of SO_4^{2-} and the lack of NO_3^- and NO_2^- in the soil samples collected close to the sources of leaking gas, indicates that available electron acceptors in the deeper portions of the microaerophilic soils are consumed in TEAP's other than methanogenesis (Table 3-6).

A number of studies have established the existence of strong redox gradients in aerobic soils (Conrad, 1995, and the references therein). The presence of such gradients suggests that aerobic and anaerobic processes coexist and that soil is a dynamic media, where conditions change rapidly when a particular substrate and/or electron acceptor is depleted (Conrad, 1995). Even in aquifers, different redox reactions are not mutually exclusive (cf. Kumaraswamy *et al.*, 2001; cf. Bjerg *et al.*, 1995). Example of the latter is the observed coexistence of methanogenic and sulphate reducing bacteria in anaerobic sediments, in spite of the fact the H_2S produced by the sulphate reducers is known to be toxic to the methanogens (Segers, 1998). Therefore, different anaerobic processes in the soil near the leaking wells may not be mutually exclusive.

The coexistence of methanogenic microorganisms and microorganisms involved in other TEAP's, however, could only be possible if these inhabit different domains in the soil or operate at different times in the year. An example of a microbiological process that appears to have well defined temporal boundaries is the precipitation of bacteriogenic calcite in the microaerophilic soil at the sites (Chapter 6). Oxygen stable isotope compositions indicate that bacteriogenic calcite precipitation is likely occurring in spring, immediately after soil at the sites thaws (Chapter 6). Low soil temperatures at that time of the year would suppress methanogenesis. Therefore, calcite precipitation is likely related to other TEA processes that may include anaerobic oxidation of CH_4, liquid hydrocarbons, or biomass.

It has been hypothesized that microorganisms and/or consortia may oxidize methane anaerobically in terrestrial settings (Sergers, 1998). Sulphate and Fe^{3+} are suspected to be involved in anaerobic oxidation of CH_4 and addition of these to anaerobic sludge and culturing media results in detectable levels of methane oxidation (Segers, 1998; Kumaraswamy *et al.*, 2001). Sulphate driven anaerobic oxidation of methane, such as this observed in marine sediments, however, has never been proven to occur in terrestrial environments. The lack of measurable SO_4^{2-} in the soil water of a sample collected at 2.0 mbs close to the casing of well A3, four years after the initial collection of a sample at this same location, indicates that all SO_4^{2-} has been reduced and that the supply of oxidized sulphur in these soils is limited and may, therefore, not sustain SO_4^{2-} reduction based bacterial community. In addition, *In vitro* assays with soil samples collected near well A3 have not shown CH_4-based sulphide production (Boetius, A. Max Plank Institute for Marine Microbiology, personal communication). It is nevertheless possible, that limited anaerobic oxidation of CH_4, driven by other electron acceptors, occur in anaerobic soils near the wells. The limited sulphur availability in the soils and the low free energy yield of SO_4^{2-} reduction driven oxidation of CH_4 render other species such as Fe^{3+} or nitrite more likely to be used as electron acceptors. Important advantages of Fe^{3+} are greater availability in soil and continuous supplementation through regeneration, especially if Fe^{2+} resides in soil as carbonate or green rust. Elevated nitrite levels in one A3 samples also suggest that denitrification is an active process in the deep soil at this site. The amino acid content of polysaccharide films can reach 30 to 38 % (cf. Hilger et al,. 2000), hence providing a source of nitrogen. Carbon source for the denitrification, however, could be either SOM or methane (cf. Kumaraswamy *et al.*, 2001).

Summary and Conclusions of Part II

Decreasing natural gas concentrations away from the leaking wells accompanied by a significant ^{13}C enrichment of residual CH_4 and C_2+ gases and a concomitant increase of the amount of CO_2 are evidence for bacterial oxidation of gaseous and liquid hydrocarbons at the three well sites. Climate in western Canada has a strong impact on the molecular and δ^{13}C composition of soil gases. Estimated natural gas consumption at the Edam sites approaches 100 % in the summer. Although low temperatures and soil freezing in winter force methanotrophic bacteria into the deeper portions of the soil, it does not reduce the fraction of methane oxidized in deeper soils near the wells. However, soil freezing reduces overall methane oxidation at the well sites by as much as 60 %.

Estimated kinetic isotope effects at the two Edam well sites demonstrate significant seasonal variability correlates negatively with soil temperature. Slopes of the correlation lines have higher values than those determined from previous studies, and for samples collected at Edam vary from 0.9 to 1.3 ε/°C. Correlation between isotope fractionation and temperature is likely related to variations in the activity of the MMO enzyme rather than changes in cellular densities. Differences between estimated $\varepsilon_{CH4-CO2}$ and $\varepsilon_{CH4m-CH4ini}$ values suggest that methanogenesis occurs in microaerophilic soil near the leaking wells.

Seasonal variability of methane and C_2+ gas ratios indicates preferential oxidation of CH_4 in summer and decoupling between CH_4 and C_2+ gases in the winter. Decoupling may be related to condensation of n-butane and subsequent partitioning of the other C_2+ gases to the liquid phase.

High natural gas concentrations, measured as far as 8.0 m from the source of leaking gas at the Maidstone monitoring site, when compared to those at the Edam sites, suggest that hydrocarbon contamination prevents natural gas oxidation by harbouring bacterial communities that out compete methanotrophic bacteria, either by consuming available oxygen or by producing toxic intermediates.

This chapter also demonstrates that a unique ecological system exists in soil near the leaking wells. Oxygen deficiency due to hydrocarbon consumption by aerobic bacteria allows a consortium of methanogenic microorganisms to produce methane. Low concentrations of organic carbon in the soils near the Edam wells indicate that fermentative bacteria metabolize lysed cells, biomass, and polysaccharide film left from the methanotrophic bacteria, therefore practically feeding from the latter. The concentrations of electron acceptors other than CO_2 (HCO_3^-) in the microaerophilic soil are low indicating that methanogenesis is the energetically favourable terminal electron acceptor process. Estimated contribution of bacteriogenic methane is not significant, however (i.e., 5 - 10 %).

In contrast, oil contamination at well A10 likely provides metabolic by-products and intermediates (mostly organic acids) of the anaerobic and aerobic degradation of oil that are fermented by hydrolytic fermenting bacteria and further reduced to acetate and hydrogen used by the methanogenic archaea. Very high H_2 concentrations measured in the microaerophilic soil near this well in winter indicate a disparity between hydrogen production and consumption likely caused by a temperature related reduction in the metabolism of methanogenic archaea at this site.

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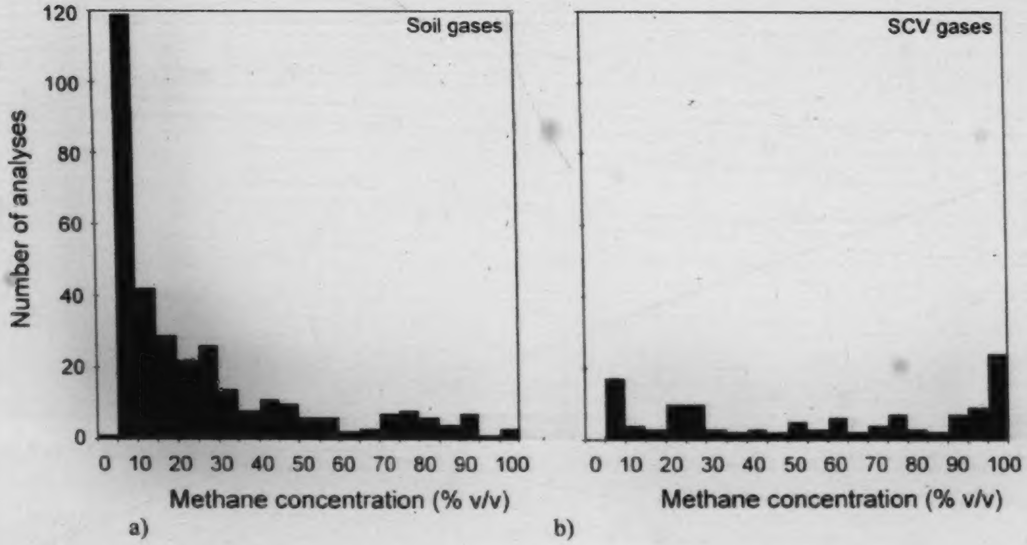


Figure 3-1 (a) Methane concentrations in soil and (b) SCV gas samples, University of Alberta gas database.

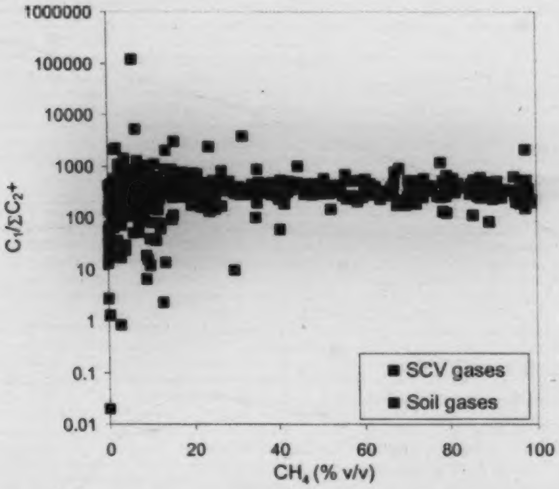


Figure 3-2 Methane concentration vs. $C_1/\Sigma C_2+$ of soil and SCV gas samples from the University of Alberta database.

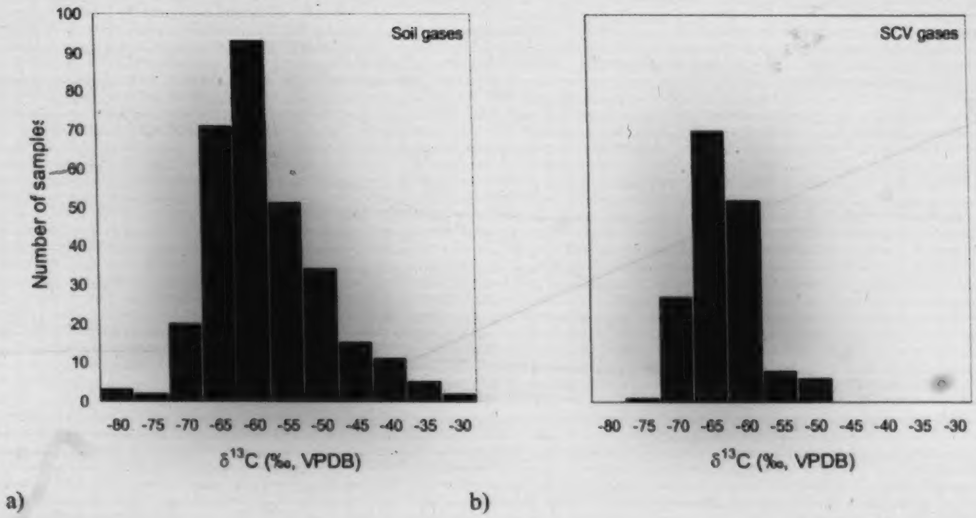


Figure 3-3 (a) Carbon stable isotope compositions of methane from soil and (b) SCV gas samples, University of Alberta database.

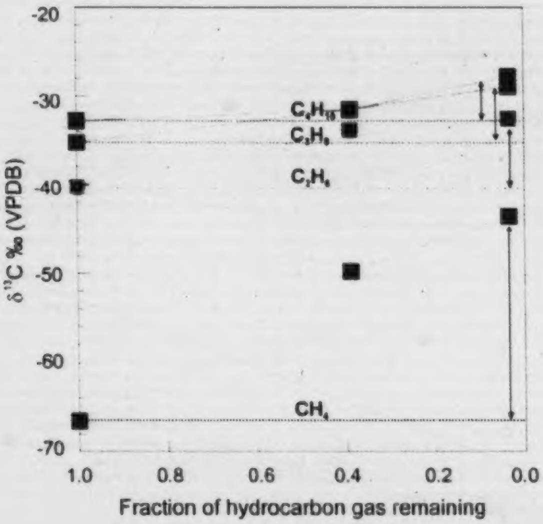
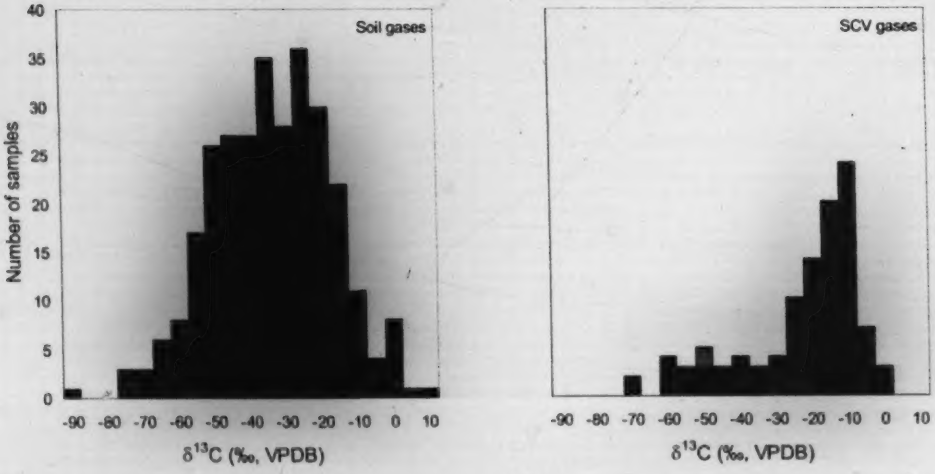


Figure 3-4 Enrichment with ^{13}C (vertical arrows) that accompanies the bacterial oxidation of the different hydrocarbon gases away from the leaking gas source. Data from soil gas samples collected at different depths and distances from the well bore at well site A3, Edam, Saskatchewan (Appendix 3).



a) b)

Figure 3-5 (a) Carbon stable isotope compositions of CO_2 of soil and (b) SCV gas sample origin, University of Alberta database.

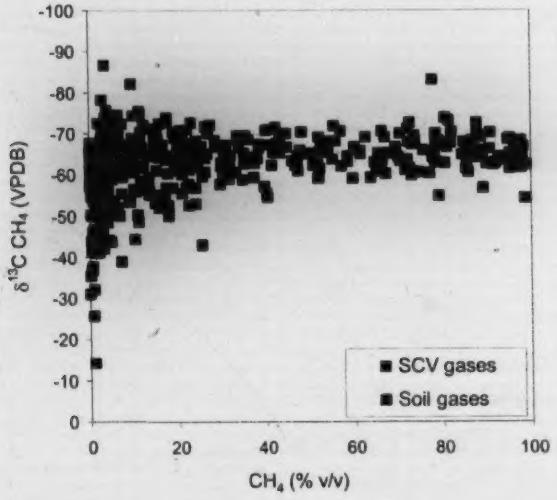


Figure 3-6 Carbon stable isotope compositions of methane vs. methane concentrations (% v/v), University of Alberta database.

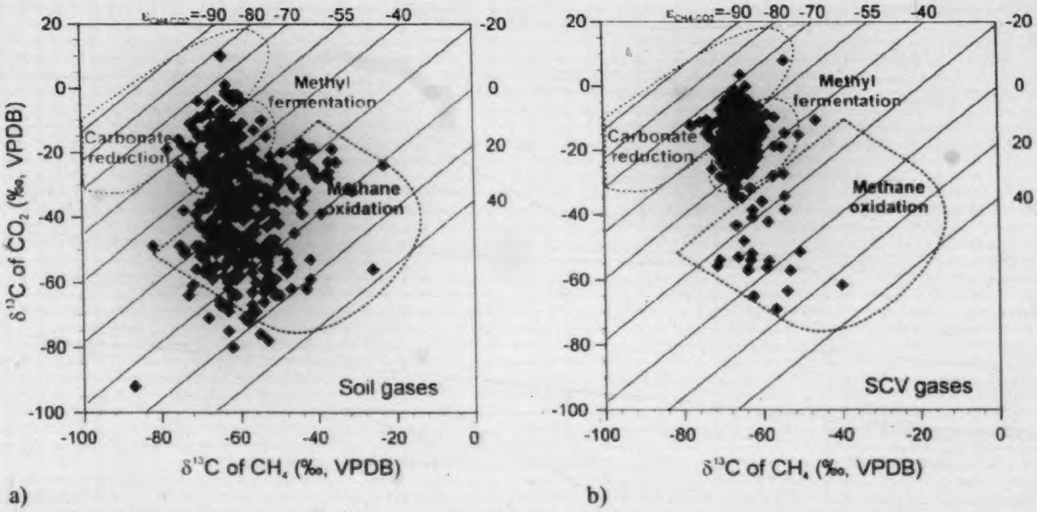


Figure 3-7 Apparent $\varepsilon_{CH4-CO2}$ values of (a) soil and (b) SCV gas samples. The fields are modified after Whiticar (1999).

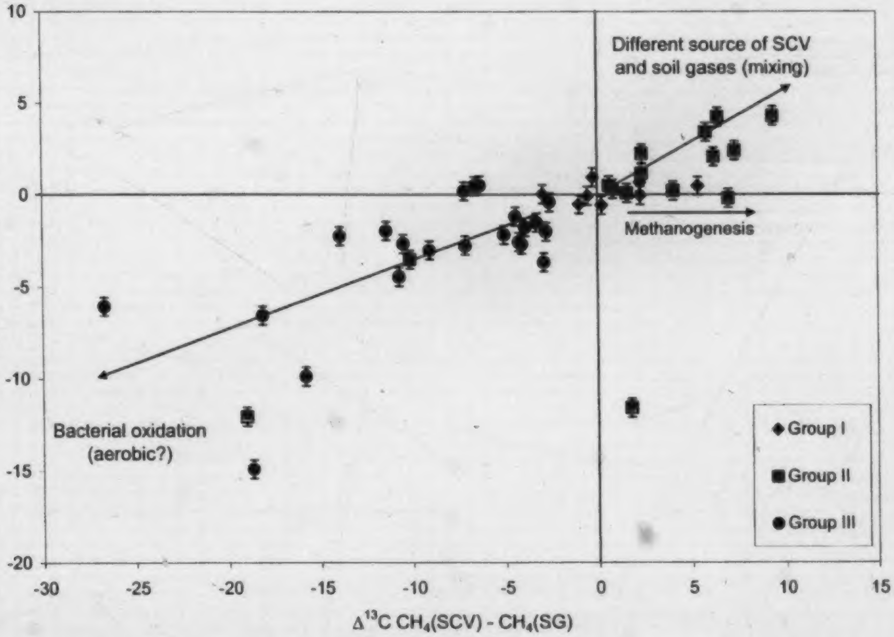


Figure 3-8 Carbon stable isotope separations ($\Delta^{13}C$) of methane vs. the $\Delta^{13}C$ of ethane from the SCV and soil gas samples collected at the same well sites.

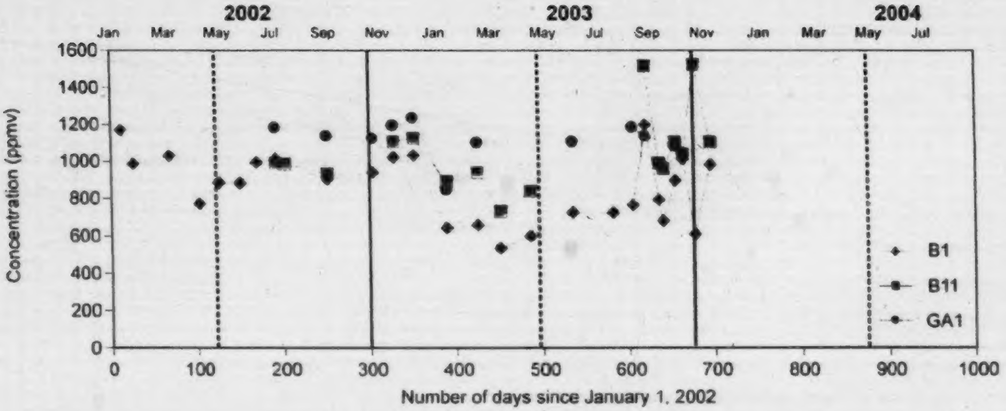


Figure 3-9 Helium concentrations (ppmv) in soil gas samples collected from the proximal probes at the three monitored well sites during almost two years of monitoring. The dashed lines connect intervals with missing data. The thick dashed and continuous vertical deep blue lines indicate thawing and freezing of the upper soil horizons, respectively. The thin blue line corresponds to a heavy rainfall on September 09, 2003 (see text).

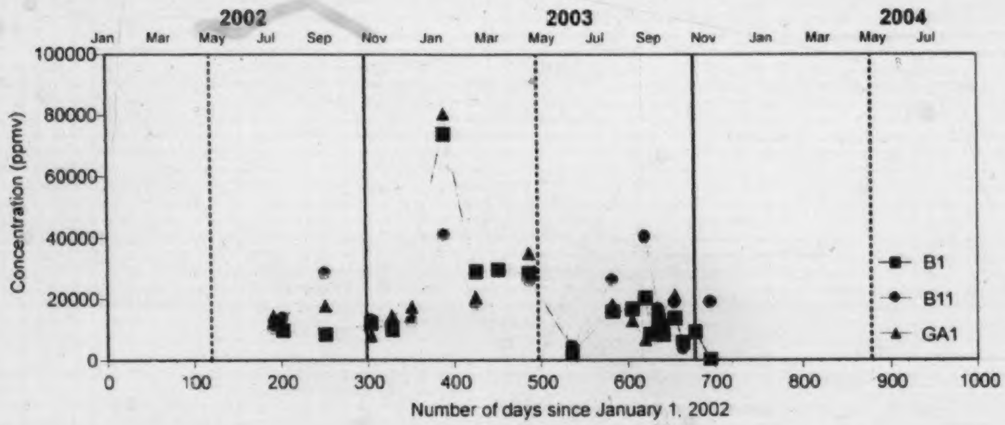


Figure 3-10 Oxygen concentrations (ppmv) in gas samples collected from the three proximal probes at the Edam and Maidstone research sites during the monitoring cycle.

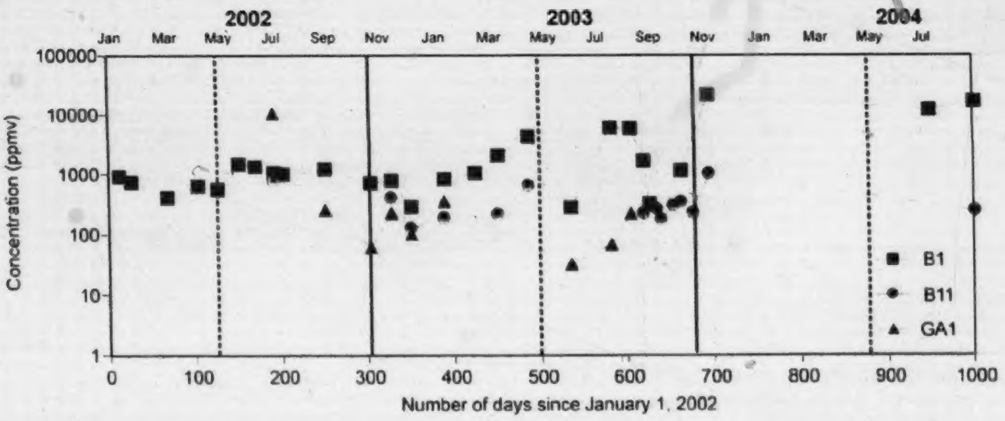


Figure 3-12 Temporal variability of carbon dioxide concentrations (ppmv) in samples collected from the proximal probes at the three research sites.

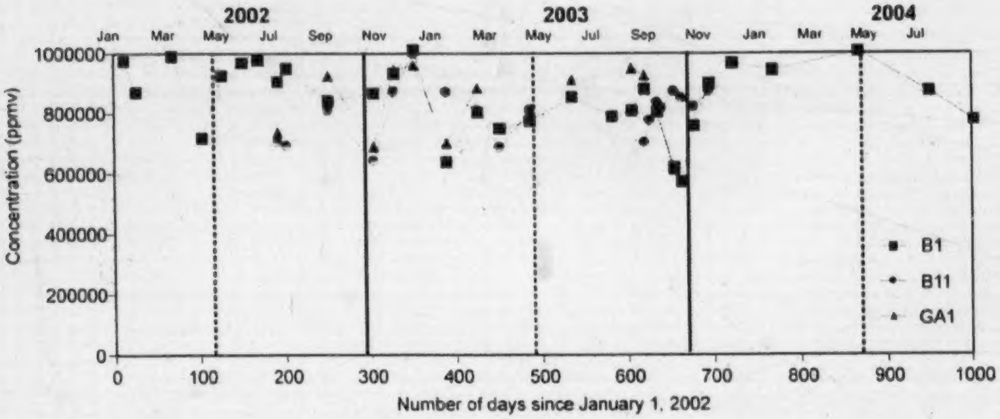


Figure 3-13 Methane concentrations (ppmv) of soil gas samples collected from the proximal probes at the three research sites.

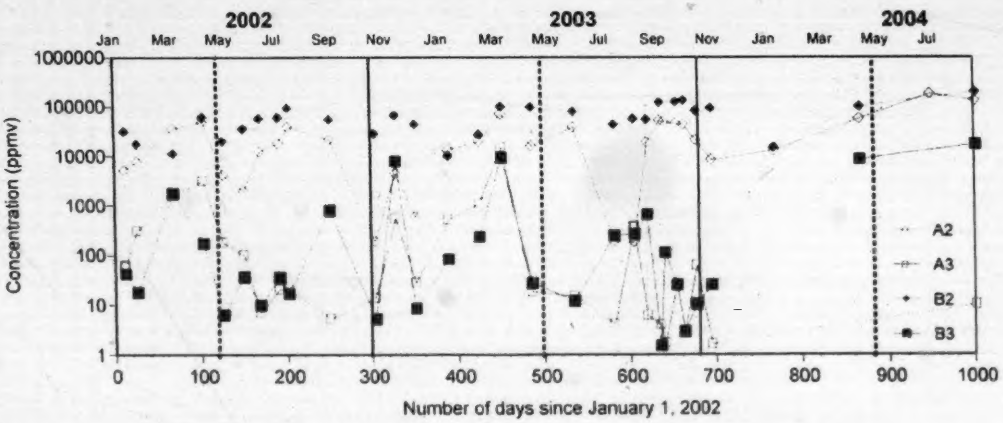


Figure 3-14 Methane concentrations (ppmv) in samples collected from the microaerophilic soil (rhombs) and oxygen rich soil (squares) at well A3, Edam.

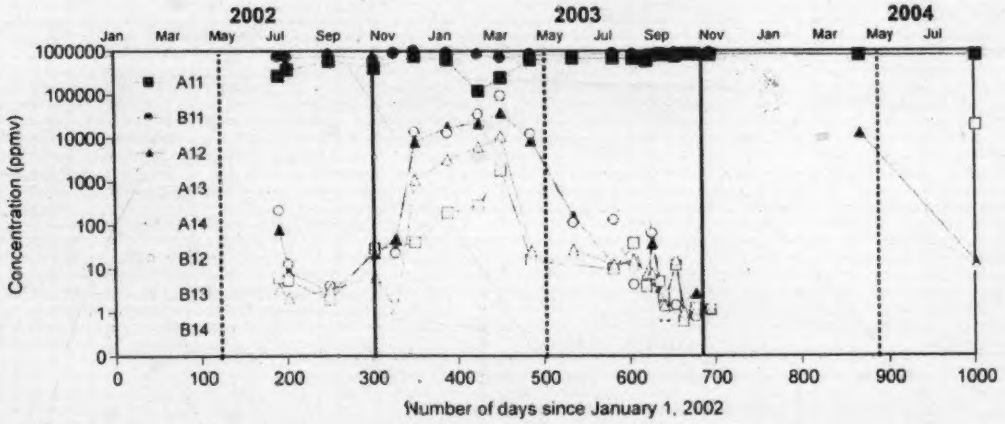


Figure 3-15 Methane concentrations (ppmv) in soil in samples collected from the microaerophilic soil (rhombs) and oxygen rich soil (squares) at well A4.

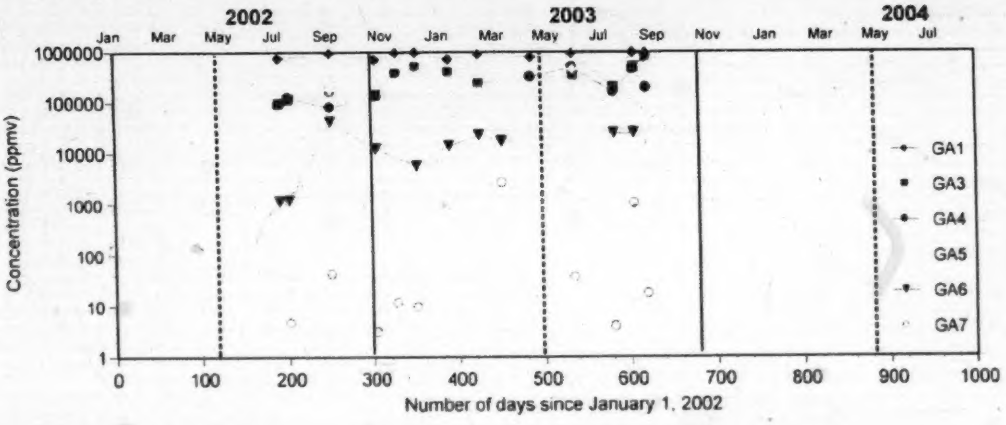


Figure 3-16 Methane concentrations (ppmv) in soil at well A10, Maidstone. For most of the year conditions at probes GA1 to GA6 are microaerophilic. The only probe installed in the oxygen-rich part of the soil is GA7.

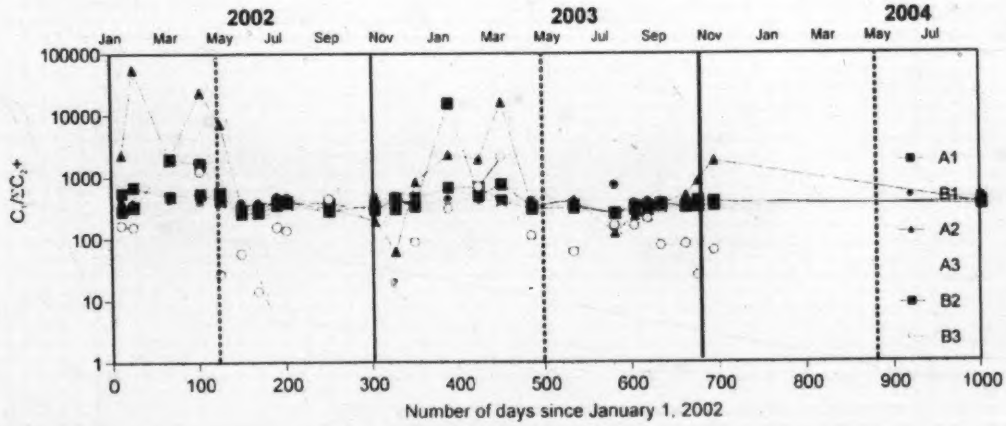


Figure 3-17 $C_1/\Sigma C_2+$ of gas samples collected from microaerophilic soil (solid symbols) and the oxygen-rich soil (hollow symbols) at well A3.

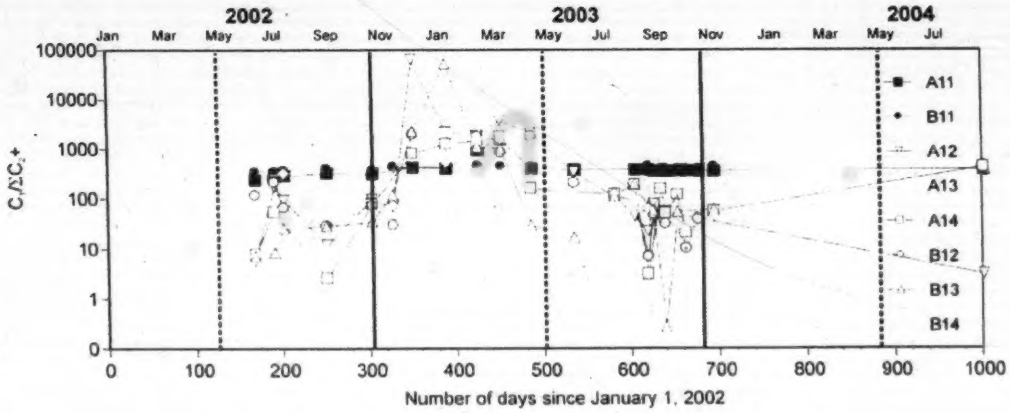


Figure 3-18 $C_1/\Sigma C_2$+ of gas samples collected from microaerophilic (solid symbols) and oxygen-rich soil (hollow symbols) at well A4.

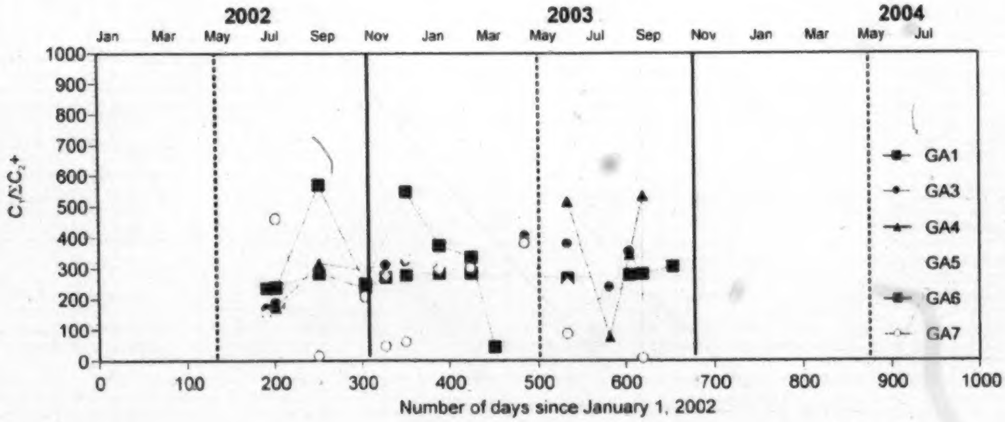


Figure 3-19 $C_1/\Sigma C_2$+ in samples collected from the microaerophilic (solid symbols) and oxygen-rich (hollow symbols) soil at well A10.

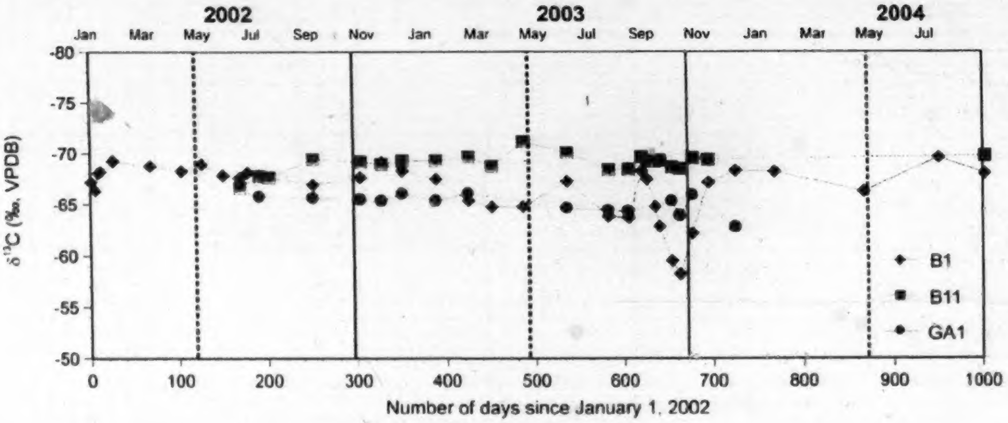


Figure 3-20 Carbon stable isotope compositions of methane in soil gas samples collected from the proximal probes at the three research sites.

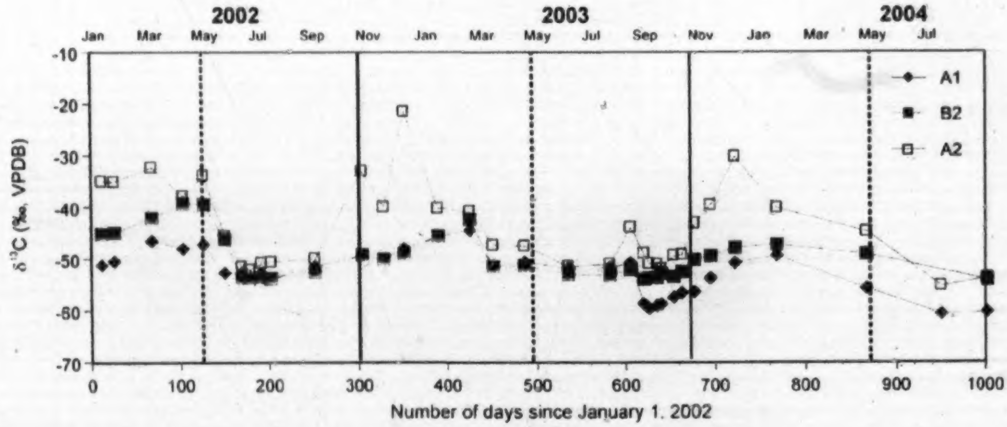


Figure 3-21 Carbon stable isotope compositions of methane in gas samples collected from the microaerophilic zone at well A3.

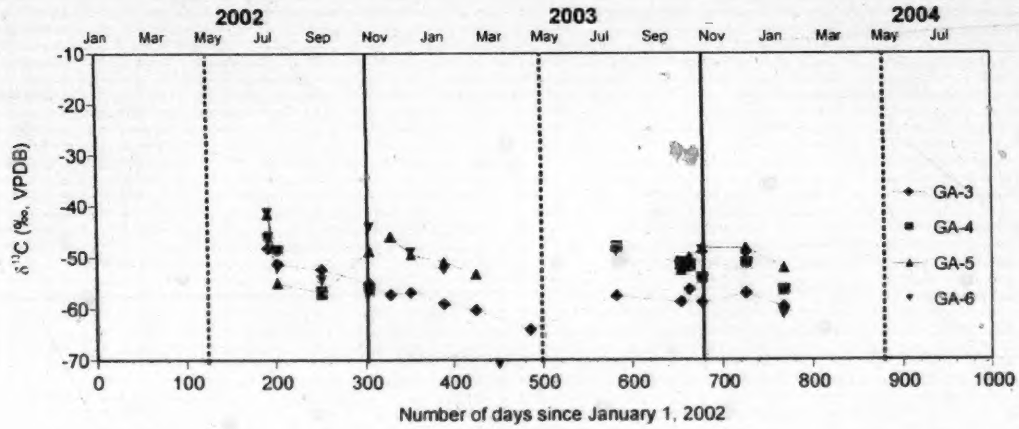


Figure 3-22 δ^{13}C of CH_4 from soil gas samples collected from the microaerophilic soil at well A10.

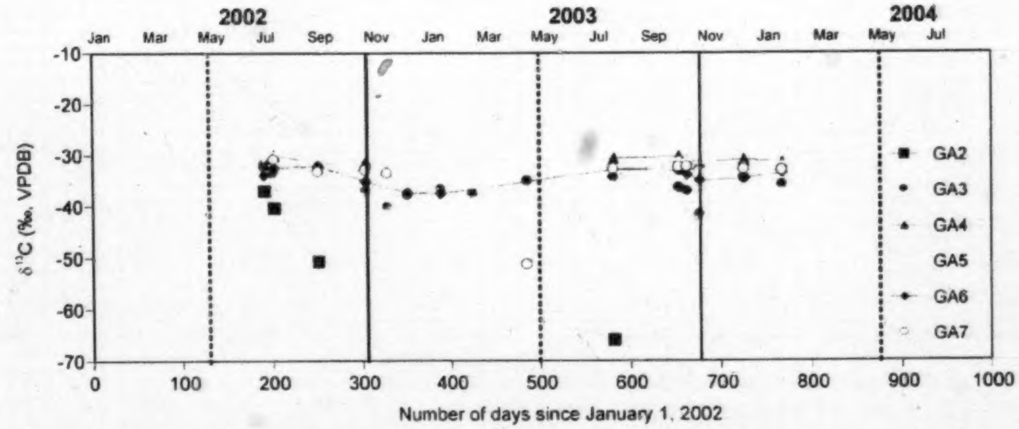


Figure 3-23 Carbon stable isotope composition of soil CO_2 from the microaerophilic (solid symbols) and oxygen-rich (hollow symbols) soil at well A1

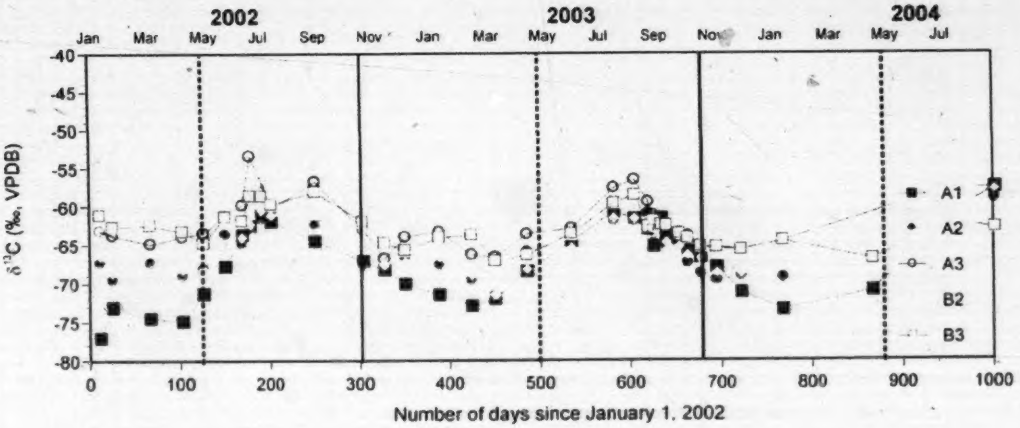


Figure 3-24 Carbon stable isotope composition of soil CO_2 from the microaerophilic (solid symbols) and oxygen-rich (hollow symbols) soil at well A3.

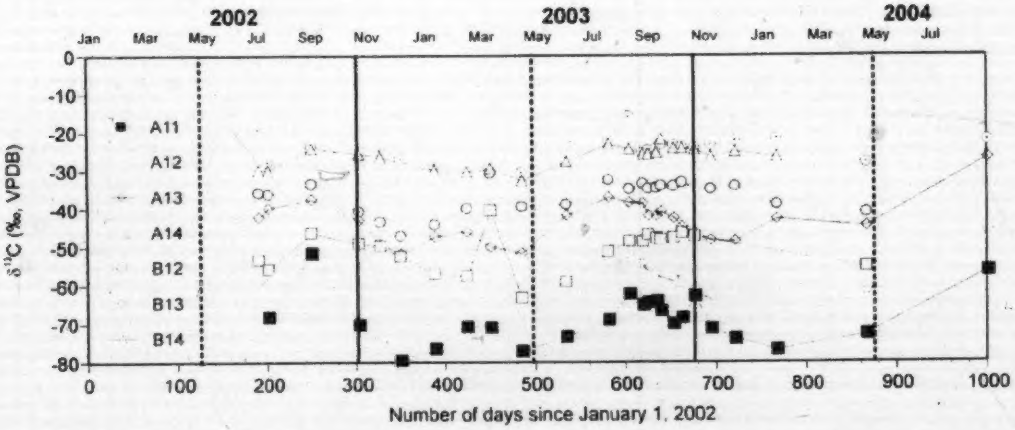


Figure 3-25 Carbon stable isotope composition of soil CO_2 from the microaerophilic (solid symbols) and oxygen-rich (hollow symbols) soil at well A4.

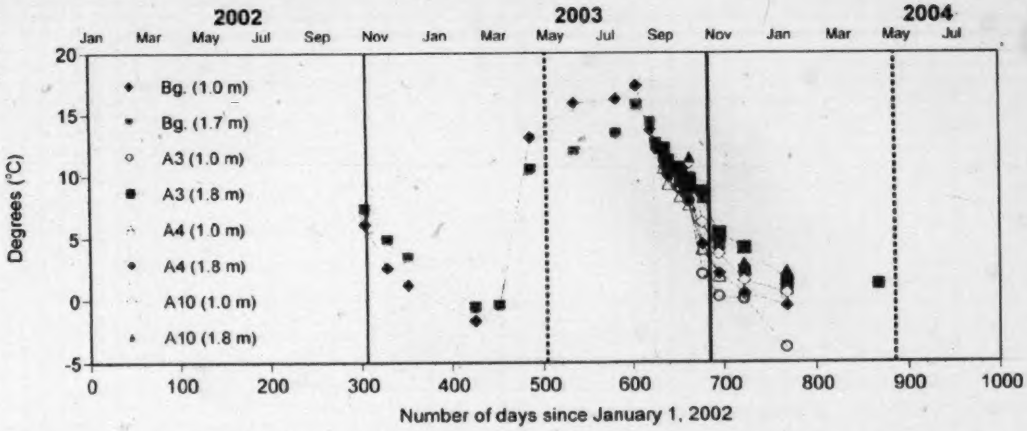


Figure 3-26 Temperature measurements (°C) at different depths in the soil at the background site and the two research sites near wells A3 and A4 at Edam and the site at Maidstone.

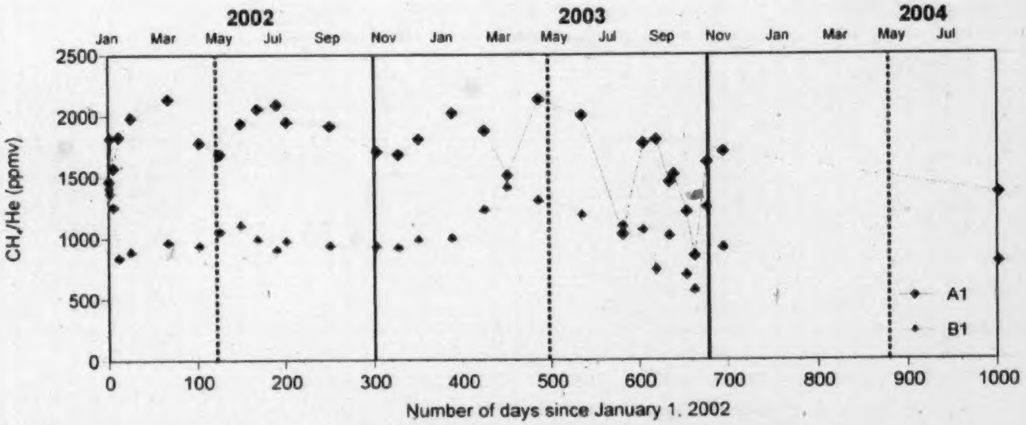


Figure 3-27 Ratio of the concentrations of methane to helium in gas samples collected from the proximal probe and probe A1at well A3. The difference between the ratios measured at the two sampling points, separated by 0.85 m of sandy soil, reaches factor of two.

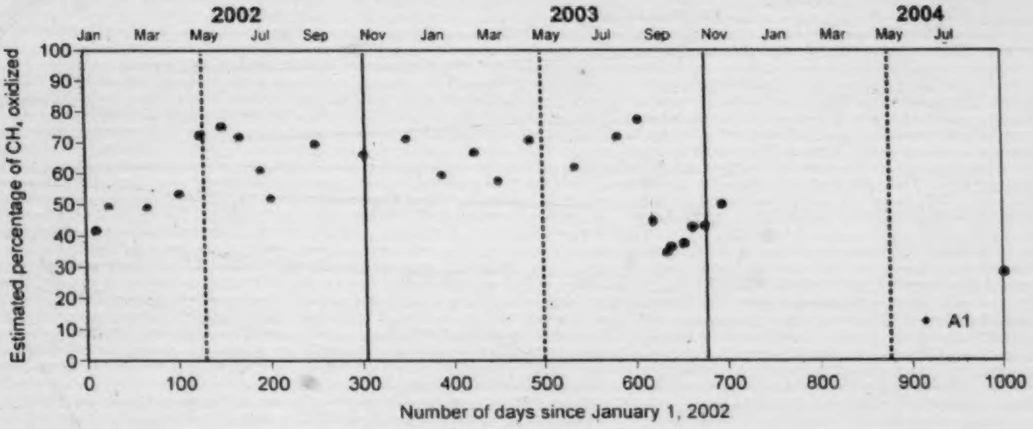


Figure 3-28 Estimated percentage of methane oxidized in shallow (1.0 m) microaerophilic soil at well A3.

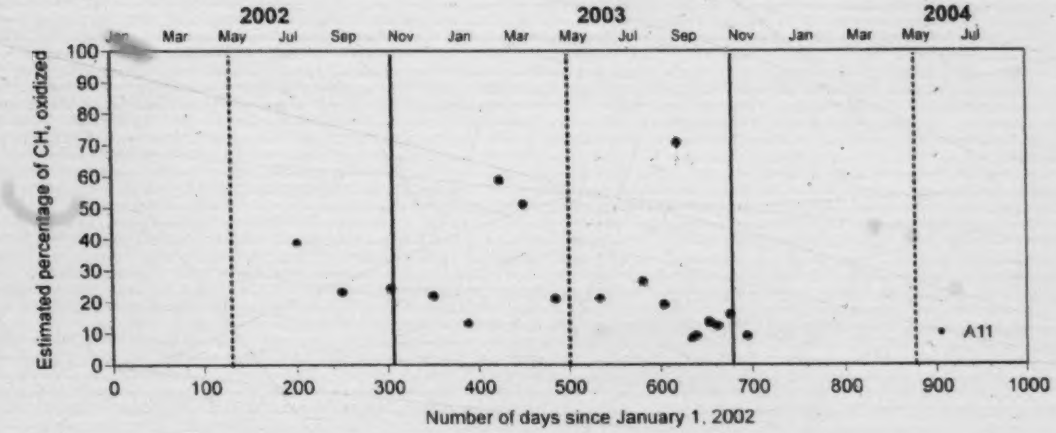


Figure 3-29 Percentage of methane oxidized in shallow (1.0 m) microaerophilic soil at well A4.

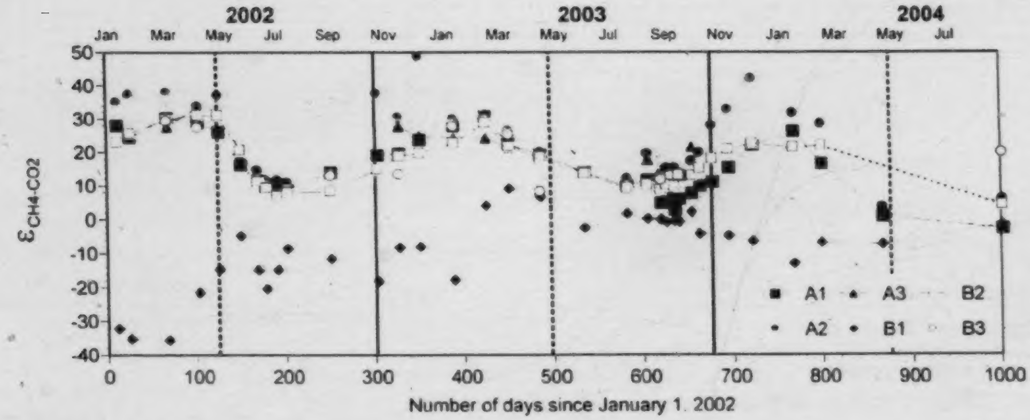


Figure 3-30 Apparent kinetic isotope effect $\varepsilon_{CH4\text{-}CO2}$ for samples collected from the microaerophilic (solid symbols) and oxygen-rich (hollow symbols) soil near well A3.

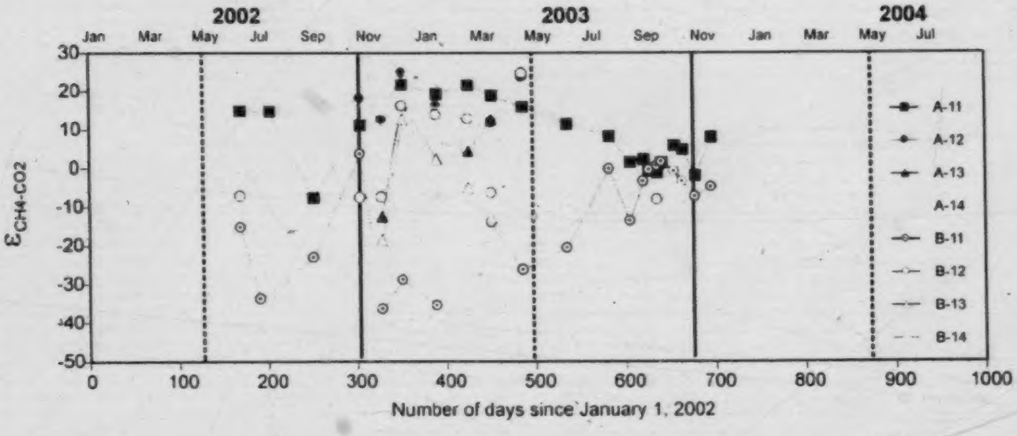


Figure 3-31 Apparent kinetic isotope effect $\varepsilon_{CH4\text{-}CO2}$ for soil gas samples collected near well A4.

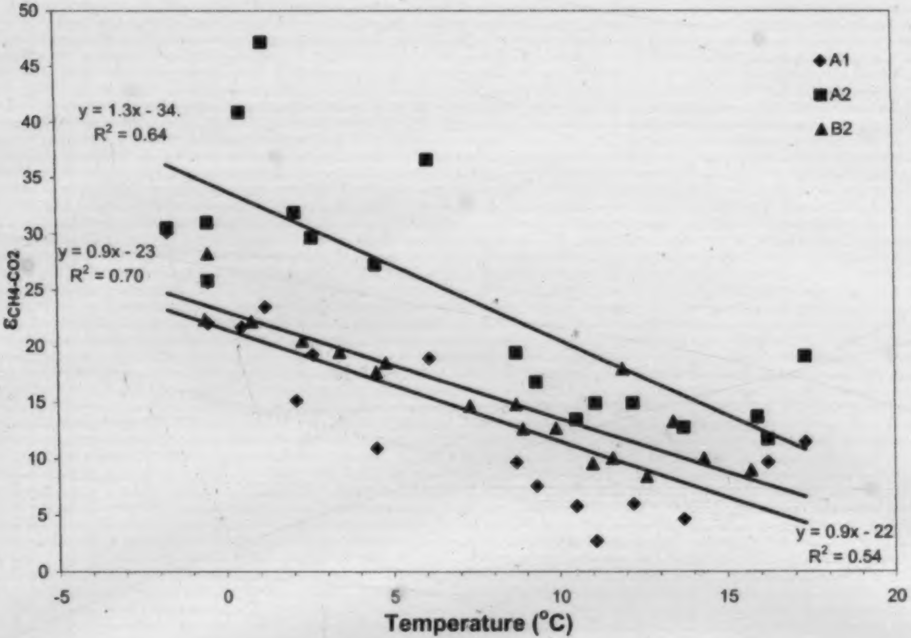


Figure 3-32 Apparent kinetic isotope effect, $\varepsilon_{CH4-CO2}$ vs. temperature for gas samples collected from different domains of the microaerophilic soil near well A3.

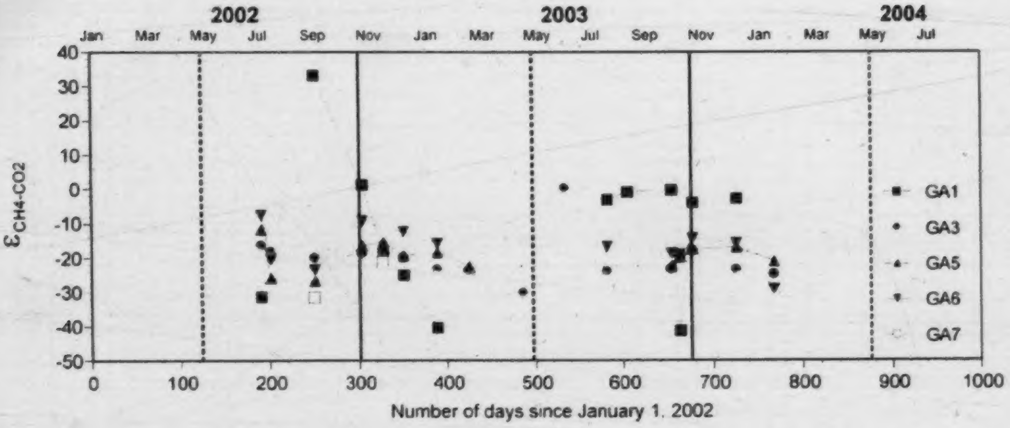


Figure 3-33 Apparent kinetic isotope effect $\varepsilon_{CH4-CO2}$ for gas sample collected from the microaerophilic soil at the research site near well A10.

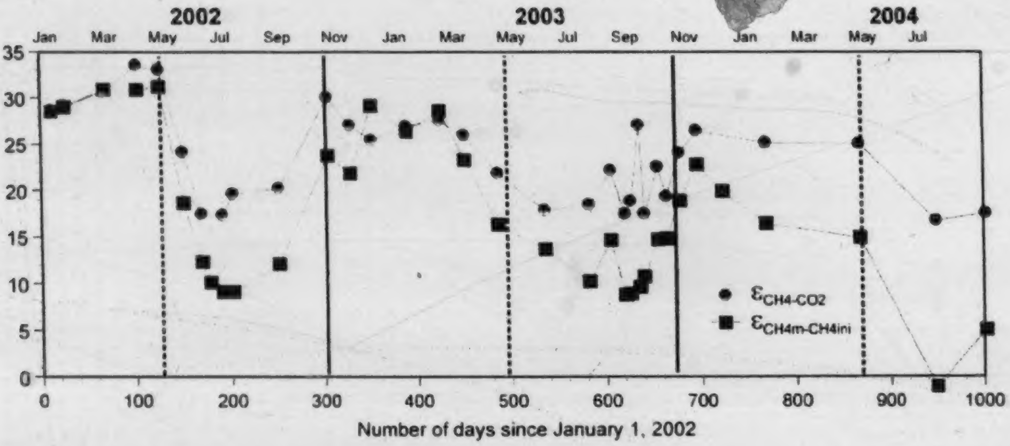


Figure 3-34 A comparison between the average $\varepsilon_{CH4m-CH4ini}$ and $\varepsilon_{CH4-CO2}$ values for samples collected from microaerophilic soil near well A3.

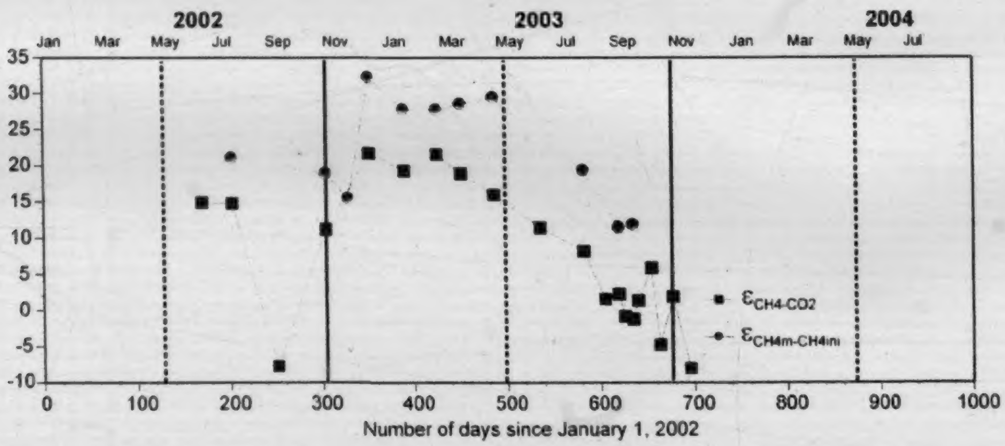


Figure 3-35 A comparison between $\varepsilon_{CH4m-CH4ini}$ and $\varepsilon_{CH4-CO2}$ values estimated for samples collected from the shallow probe A11 at the research site near well A4.

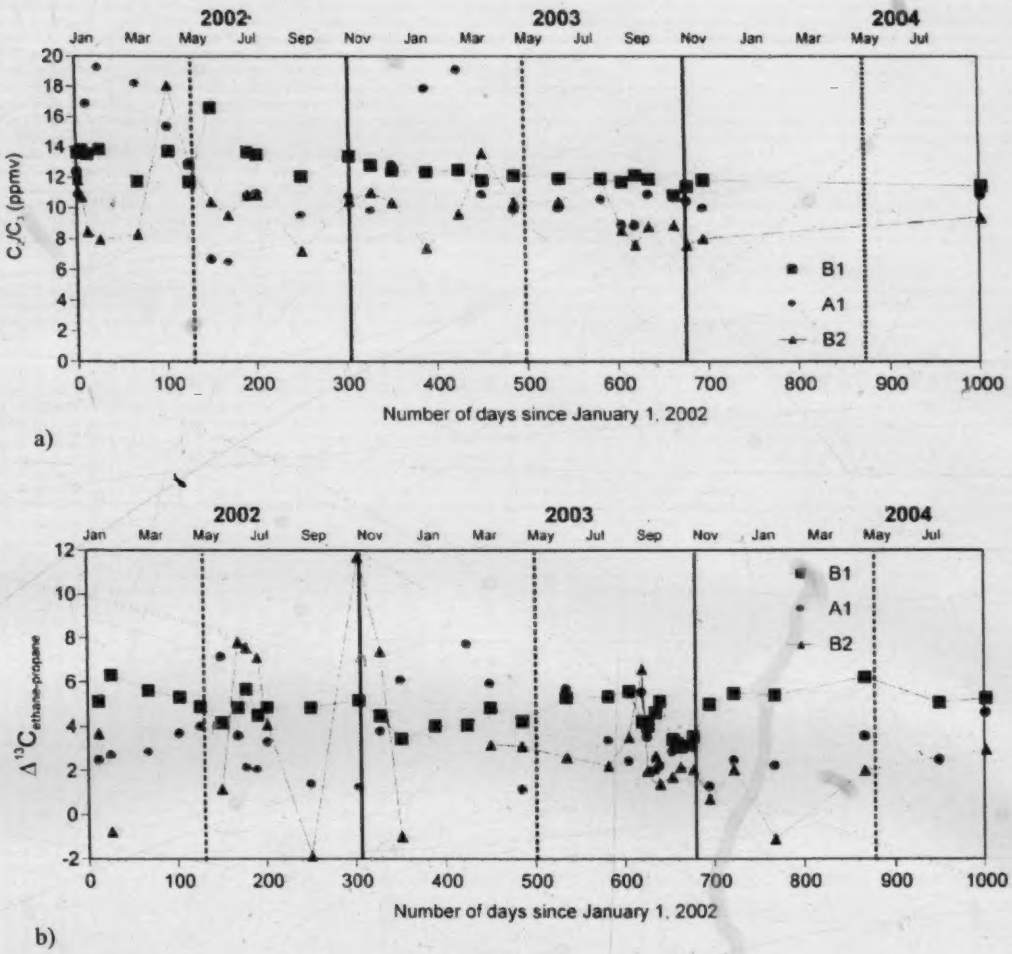
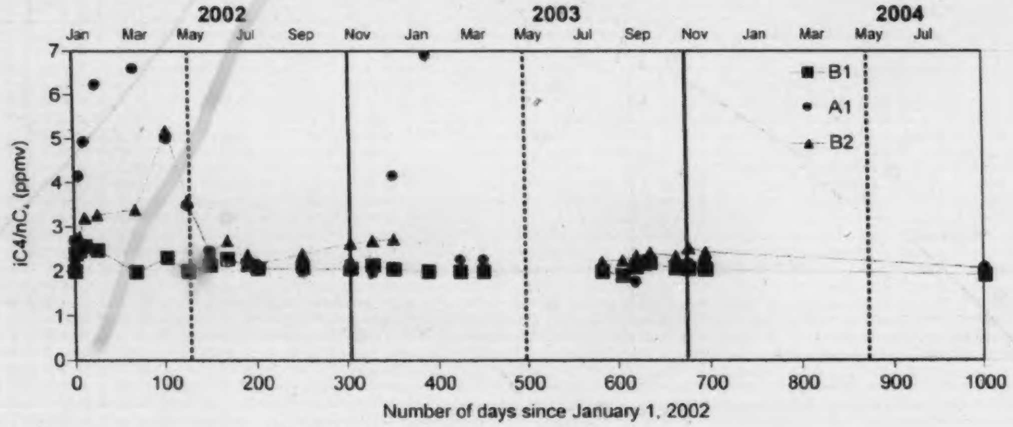
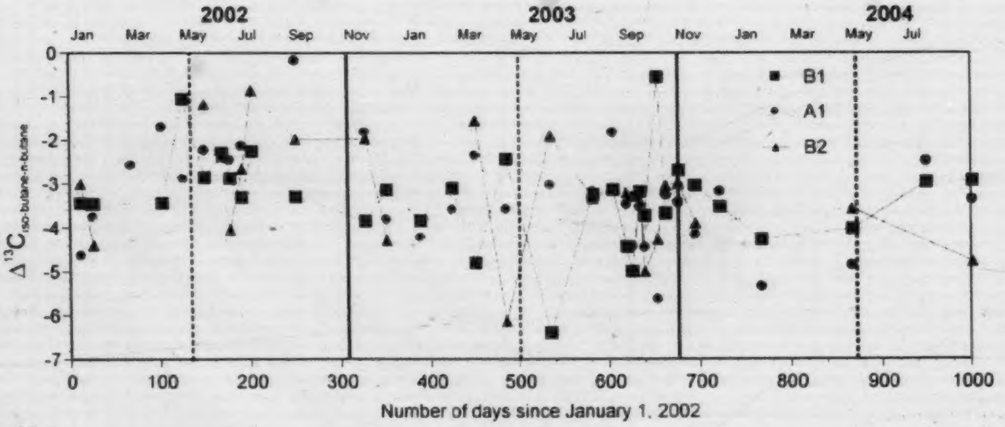


Figure 3-36 (a) Molecular ratios $C_{ethane-propane}$ and (b) isotope separations between ethane and propane $\Delta^{13}C_{ethane-propane}$ in soil gases collected at well A3.



a)



b)

Figure 3-37 (a) Molecular ratios and (b) isotope separations between iso-butane and normal butane in soil gases collected at well A3.

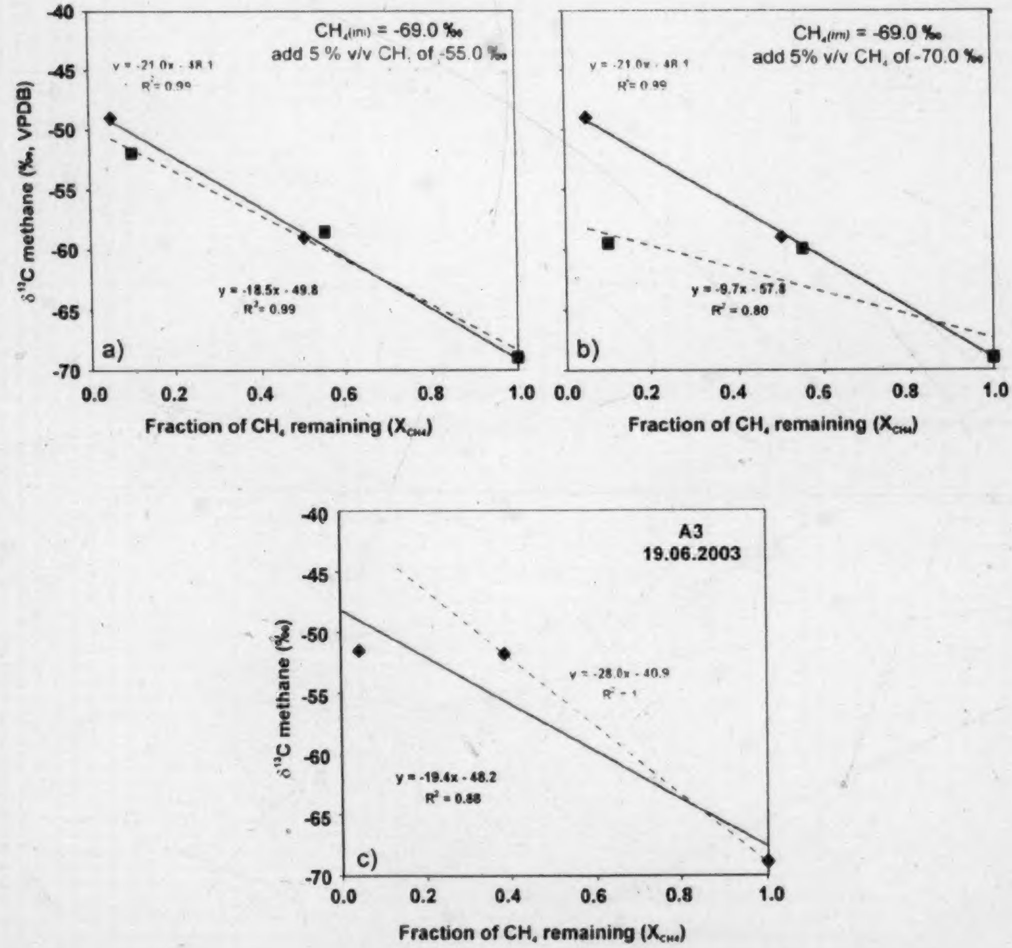


Figure 3-38 Carbon stable isotope composition of methane vs. the fraction of methane remaining. The addition of 5 % v/v methane having δ^{13}C of -55 ‰ (a) and -70 ‰ (b) shifts the "original" values (rhombs) to new positions (squares). Figure 3-38(b) mimics well the distribution of measured δ^{13}C compositions and estimated fractions of methane oxidized at wells A3 (c) in the summer.

Table 3-1 Statistical summary of the concentrations (ppmv) and/or $\delta^{13}C$ compositions (‰, VPDB) of soil and SCV gas samples from the University of Alberta Database.

Soil Gas samples	C_1	C_2	C_3	iC4	nC4	C_{5+}	CO_2	He	H_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$
Mean	**285571**	**626**	**83**	37	**14**	**886**	**29148**	**41**	**67**	**-60.3**	**-40.9**	**-34.7**	**-30.0**	**-30.7**	**-36.5**
Standard Error	13703	48	10	5	3	433	4990	12	26	0.5	0.4	0.3	0.2	0.4	1.0
Median	102099	274	28	9	3	11	13300	13	5	-61.9	-41.1	-35.7	-30.4	-30.7	-35.6
Mode	36200	0	0	0	0	0			3	-64.7	-47.9	-38.6	-30.9	-35.8	-24.6
Standard Deviation	**241265**	**837**	**179**	**84**	**50**	**5628**	**34208**	**48**	**184**	**8.9**	**6.5**	**5.3**	**3.1**	**5.1**	**16.4**
Skewness	1	2	7	5	10	8	2	1	3	1.1	0.1	0.9	0.3	0.4	-0.2
Range	975180	6111	1900	782	700	56800	155604	136	919	72.4	38.8	37.5	19.1	24.1	101.2
Minimum	**330**	**0.8**	**0.2**	**0.1**	**0.1**	**0.3**	**84**	**0.2**	**0.2**	**-86.6**	**-59.2**	**-50.6**	**-39.3**	**-41.1**	**-91.6**
Maximum	**975510**	**6111**	**1900**	**782**	**700**	**56800**	**155688**	**136**	**919**	**-14.2**	**-20.4**	**-13.1**	**-20.2**	**-17.0**	**9.6**
Count	310	310	308	308	308	169	47	16	51	309	293	273	234	188	293
Confidence Level(95.0%)	26963	93	20	9	6	855	10044	26	52	1.0	0.7	0.6	0.4	0.7	1.9

SCV gas samples	$C_{1\,ppm}$	$C_{2\,ppm}$	$C_{3\,ppm}$	$C_{4\,ppm}$	$C_{5\,ppm}$	$C_{6+\,ppm}$	$CO_{2\,ppm}$	He ppm	$H_{2\,ppm}$	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$
Mean	**518114**	**1557**	**201**	**71**	**28**	**43**		**931**	**199**	**-65.7**	**-44.0**	**-37.3**	**-31.4**	**-32.9**	**-25.7**
Standard Error	26630	116	26	16	7	27		249	78	0.4	0.5	0.3	0.2	0.4	1.6
Median	546236	1200	116	37	11	4		636	52	-66.0	-43.3	-37.9	-31.7	-33.8	-20.0
Mode	175567	1500	100	0	0	0		700	200	-64.9	-41.4	-35.2	-30.6	-41.4	-25.8
Standard Deviation	**343108**	**1492**	**322**	**202**	**85**	**199**		**1430**	**397**	**4.5**	**6.1**	**4.2**	**2.6**	**4.3**	**16.6**
Skewness	0	2	5	8	7	6		3	4	0.8	0.0	0.7	0.6	0.5	-1.0
Range	989340	9911	2647	2136	707	1419		6468	1962	24.7	33.3	19.5	17.0	20.7	71.9
Minimum	**83**	**14**	**2**	**0.03**	**0.07**	**0.19**		**0.02**	**0.7**	**-75.3**	**-60.0**	**-45.7**	**-38.4**	**-41.4**	**-73.3**
Maximum	**989423**	**9925**	**2647**	**2136**	**707**	**1419**		**6468**	**1962**	**-50.7**	**-26.7**	**-26.2**	**-21.4**	**-20.7**	**-1.3**
Count	166	165	154	152	150	56		33	26	165	164	161	150	131	107
Confidence Level(95.0%)	52580	229	51	32	14	53		507	160	0.7	0.9	0.7	0.4	0.7	3.2

Table 3-2. Concentrations (ppmv), $\delta^{13}C$ compositions (‰, VPDB) and ratios of hydrocarbon and CO_2 gases from SCV and SG samples collected at the same well site

Date	Type	Well	LSD						C_1	C_2	C_3	C_4	C_4	C_{6+}	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$	$C_1/(\Sigma C_2+$	C_2/C_3	iC_4/nC_4	ΔC_2-C_3	ΔiC_4-nC_4
GROUP I																									
01.08.2000	SCV	b5	0	5	12	48	23	W3M	920877	3051	358	145	35		-63.0	-41.7	-35.8	-31.1	-36.0	-18.5	257	8.5	4.2	5.9	-4.8
01.08.2000	SG	b5	0	5	12	48	23	W3M	417748	1280	146	60	14	5	-65.3	-41.7	-35.4	-30.4		-34.7	278	8.8	4.2	6.2	
17.07.2003	SCV	A		7	11	47	5	W4M	667148	2118	196	47	20	18	-63.6	-46.7	-39.0	-33.6	-35.2		280	10.8	2.4	7.7	-1.6
17.07.2003	PVC	A		7	11	47	5	W4M	461080	1446	132	32	13	13	-63.4	-47.7	-39.7	-31.3		-66.5	284	10.9	2.4	8.0	
02.08.2000	SCV	1d9	0	9	11	48	23	W3M	498199	1476	152	57	14		-65.0	-42.4	-37.7	-33.4	-38.7	-4.4	293	9.7	4.2	4.6	-5.3
02.08.2000	SG	1d9	0	9	11	48	23	W3M	657473	2018	221	101	23	24	-65.2	-41.8	-36.6	-32.7	-37.9	-10.8	278	9.1	4.3	5.2	-5.2
13.09.2000	SCV	a9	0	9	12	51	24	W3M	948388	1319	136	93	12		-68.6	-55.2	-41.7	-34.0			608	9.7	7.7	13.6	
13.09.2000	SG	a9	0	9	12	51	24	W3M	807952	1180	125	70	9		-73.9	-55.7	-41.6	-32.0	-33.3		583	9.4	7.4	14.1	-1.4
01.08.2000	SCV	c5	0	5	12	48	23	W3M	573202	1848	203	80	19		-62.0	-40.8	-35.4	-31.2	-34.4	-10.6	267	9.1	4.1	5.4	-3.1
01.08.2000	SG	c5	0	5	12	48	23	W3M	205577	658	81	34	9	7	-64.3	-41.5	-35.7	-31.4	-32.7	-48.9	263	8.2	4.0	5.8	-1.3
12.09.1999	SCV		0	10	17	48	5	W4M	981200	3382	350	70	35		-65.1	-50.2	-41.4	-35.1	-35.3		256	9.7	2.0	8.8	-0.2
12.09.1999	SG		0	10	17	48	5	W4M	255690	700	85	22	12		-64.1	-49.7	-41.4	-34.5	-36.7	-35.2	312	8.2	1.8	8.3	-2.2
	SCV	15a	0	15	22	54	2	W4M	571291	993	87	50	7		-70.5	-53.2	-43.2	-33.8	-37.1		502	11.5	7.4	10.0	-3.4
04.10.1999	BBL	15A	0	15	22	54	2	W4M	426929	763	65	15	5		-67.5	-53.3	-42.9	-32.7	-29.8	-14.9	503	11.7	3.3	10.4	2.9
19.09.1999	SCV	2D13	0	13	11	48	23	W3M	978195	4210	491	77	36		-64.8	-41.1	-34.2	-28.0	-29.3		203	8.6	2.1	6.9	-1.3
19.09.1999	SG	2D13	0	13	11	48	23	W3M	954849	3631	422	66	31		-64.3	-41.1	-34.5	-28.6	-32.2	9.6	230	8.6	2.1	6.5	-3.6
GROUP II																									
Different gases																									
2001	SCV			2	27	49	22	W3M	952332	2639	185	49	12		-68.9	-43.1	-41.3	-35.0	-38.6	-14.5	330	14.3	4.2	1.8	-3.6
23.06.2003	SCV			2	27	49	22	W3M	229838	549	40	10	3		-72.6	-45.7	-41.8	-35.4			382	13.9	3.9	3.9	
21.12.2003	SCV			2	27	49	22	W3M	547327	1441	109	25	8	3	-68.2	-42.6	-40.4	-33.2	-37.2		346	13.3	3.2	2.2	-4.0
	SCV	C4	0	4	12	48	23	W3M	965320	3058	388	162	42		-63.7	-41.6	-35.8	-30.7	-35.0		264	7.9	3.8	5.8	-4.3
31.07.2000	SG	c4	0	4	12	48	23	W3M	351007	966	109	40	8		-65.3	-41.7	-37.1	-33.0	-39.1	-29.0	313	8.9	4.8	4.6	-6.1
	SCV	b3	0	3	12	48	23	W3M	552462	1756	225	93	29		-63.8	-41.7	-36.6	-32.4	-31.6	-13.9	263	7.8	3.2	5.1	0.8
27.07.2000	SG	b3	0	3	12	48	23	W3M	44229	131	15	4	1		-53.7	-38.2	-37.8	-35.8	-36.2	-38.8	293	8.6	4.9	0.4	-0.4
20.11.2001	SCV	c		5	14	48	23	W3M	974766	3650	355	68	30		-63.9	-40.0	-33.7	-29.9	-32.4	-6.6	238	10.3	2.3	6.3	-2.4
20.11.2001	SG	c		5	14	48	23	W3M	176980	530	55	11	6	9	-70.3	-44.2	-36.1	-31.3	-30.2	-9.0	294	9.7	1.9	8.1	1.0
04.08.2000	SG	c5	0	5	14	48	23	W3M	240722	854	124	59	16	25	-65.4	-41.2	-33.8	-28.7	-34.1	-14.3	229	6.9	3.6	7.3	-5.4
30.09.1999	SCV	2B14	0	14	11	48	23	W3M	615791	1993	213	29	15		-65.0	-41.6	-34.3	-29.6	-28.8	-14.1	274	9.3	2.0	7.3	0.8
30.09.1999	SG	2B14	0	14	11	48	23	W3M	56130	121	13	3	2	7	-74.3	-45.9	-37.2	-27.2		-49.8	405	9.7	1.9	8.7	
07.09.2000	SCV	11c	0	11	29	46	6	W4M	952945	3849	663	303	75		-65.2	-41.5	-32.6	-29.1	-29.9		195	5.8	4.1	8.8	-0.8
11.09.1999	SG		0	11	29	46	6	W4M	723198	3335	490	83	46	14	-71.0	-44.9	-34.9	-31.1	-29.9	-38.6	183	6.8	1.8	10.0	1.2
07.09.2000	SG	11c	0	11	29	46	6	W4M	718409	2924	496	238	56	15	-61.2	-40.2	-32.1	-29.5	-30.2	-35.5	193	5.9	4.3	8.1	-0.7
	SCV	c16	0	16	11	48	23	W3M	846368	2576	276	99	25		-64.9	-41.1	-34.8	-29.4	-31.5	-10.8	284	9.3	4.0	6.4	-2.1
02.08.2000	SG	c16	0	16	11	48	23	W3M	88953	259	30	10	3		-67.2	-42.3	-34.3	-29.4	-35.6	-26.6	295	8.7	3.1	8.0	-6.2
01.06.2001	SCV			16	24	44	1	W4M	960388	4322	313	69	22		-65.1	-37.9	-34.6	-21.4	-31.7	-26.6	203	13.8	3.1	3.3	-10.3
01.06.2001	SG			16	24	44	1	W4M	7574	30	0	1	0		-46.1	-25.8				-44.7	242	121.5	16.8		

Table 3-2. Concentrations (ppmv), $\delta^{13}C$ compositions (‰, VPDB) and ratios of hydrocarbon and CO_2 gases from SCV and SG samples collected at the same well site (cont.)

Date	Type	Well	LSD						C_1	C_2	C_3	C_3	C_2	C_{6+}	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$	$C_1/(\Sigma C_{2+}$	C_2/C_3	iC_4/nC_4	ΔC_2-C_3	ΔiC_4-nC_4
GROUP II **Methanogenesis (?)**																									
	SCV	10d	0	10	36	62	7	W4M	989423	4033	421	91	33		-62.4	-45.5	-40.3	-32.5	-37.3	-38.5	216	9.6	2.8	5.2	-4.8
27.04.1998	SG	10d	0	10	36	62	7	W4M	37011	83	6	2	1		-68.6	-47.6	-40.2	-32.0		-53.2	402	13.8	3.4	7.4	
	SCV	1c	0	1	36	47	5	W4M	954117	2440	265	126	26		-63.3	-48.6	-41.2	-33.2	-37.4		334	9.2	4.8	7.4	-4.1
25.08.2000	SG	1c	0	1	36	47	5	W4M	189361	479	78	11	5		-70.3	-48.4	-38.3	-31.7	-35.5	-51.9	331	6.2	2.3	10.1	-3.8
	SCV	c6	0	6	12	48	23	W3M	951440	3127	363	150	34		-61.4	-41.4	-37.6	-34.2	-39.6		259	8.6	4.4	3.8	-5.5
01.08.2000	SG	c6	0	6	12	48	23	W3M	98122	296	38	8	5	12	-68.8	-43.8	-36.0	-30.9	-36.4	-24.4	283	7.9	1.7	7.8	-5.5
2000	SCV	2D8	0	8	11	48	23	W3M	888590	3026	337	135	29		-64.9	-40.9	-37.0	-34.3	-39.9		252	9.0	4.6	3.9	-5.6
26.07.2000	SG	2d8	0	8	11	48	23	W3M	311303	961	118	49	13		-67.3	-43.1	-36.7	-30.5	-34.0	-4.6	273	8.2	3.9	6.5	-3.4
05.10.2000	SG	2D8	0	8	11	48	23	W3M	96782	352	51	25	7	4	-63.7	-42.6	-38.0	-34.1	-38.1	-33.2	223	6.9	3.6	4.5	-4.0
13.07.01	SG	2d8	0	8	11	48	23	W3M	1114	7	1	0	0		-67.7					-7.5	141	8.8	1.0		
	SCV	16D	0	16	32	55	4	W4M	980321	4114	344	45	20	7	-61.9	-41.0	-33.8	-29.0	-31.2	-11.3	217	[illegible]	2.3	7.2	-2.2
13.10.1999	SG	16D	0	16	32	55	4	W4M	759954	1706	105	9	3	1	-65.9	-41.3	-33.6	-33.7		-50.6	417	16.2	3.2	7.7	
16.04.2000	SCV	6b	0	6	21	54	5	W4M	807240	1999	223	94	20		-62.8	-48.6	-41.0	-33.3	-36.8	-51.9	346	9.0	4.7	7.6	-3.5
16.04.2000	SG	6b	0	6	21	54	5	W4M	706815	1542	166	66	13		-63.4	-49.1	-39.5	-32.0	-37.0	-1.7	395	9.3	4.9	9.6	-5.1
	SCV	B4	0	4	12	48	23	W3M	780700	2700	400	0	0	0	-64.2	-41.7	-37.3	-32.8	-38.1		252	6.8		4.4	-5.3
27.07.2000	SG	b4	0	4	12	48	23	W3M	72880	199	23	9	2	0	-65.0	-42.0	-37.9	-31.0	-32.3	-67.4	313	8.8	4.4	4.2	-1.3
15.05.1998	SCV	b12	0	12	12	48	23	W3M	484672	1477	163	63	13		-65.0	-43.3	-39.7	-33.6	-35.1	-12.1	282	9.0	4.7	3.6	-1.5
01.08.2000	SG	b12	0	12	12	48	23	W3M	59706	33	15	242	49	234	-66.8	-31.8	-25.5	-24.4	-21.4	-18.5	178	2.3	4.9	6.3	3.1
GROUP II **Summer**																									
19.07.2000	SCV	a1	0	1	6	47	23	W3M	907595	2515	277	91	24		-66.2	-43.6	-36.1	-30.6	-28.9		312	9.1	3.8	7.4	1.7
19.07.2000	SG	a1	0	1	6	47	23	W3M	397812	1284	155	55	14	6	-57.2	-40.6	-35.1	-29.7	-35.3	-55.4	264	8.3	3.8	5.5	-5.6
22.07.2003	SCV			1	33	42	1	W4M	855140	6837	713	133	69	33	-61.5	-31.5	-26.8	-26.5	-26.3		110	9.6	1.9	2.7	0.2
22.07.2003	SG			1	33	42	1	W4M	347756	2980	327	66	31	18	-58.7	-29.5	-26.7	-26.3	-26.3	-54.3	102	9.1	2.1	2.8	0.0
	SCV		0	15	23	68	21	W4M	202837	472	35	21	5		-63.6	-45.1	-39.0	-31.5	-32.5	-27.3	380	13.3	4.3	8.2	-0.9
23.07.2000	SG		0	15	23	68	21	W4M	482877	993	58	16	7		-70.4	-49.8	-39.9	-32.4	-37.5	-42.8	450	17.1	2.3	9.9	-5.1
23.07.2000	SG		0	15	23	68	21	W4M	789939	1776	117	34	24	7	-67.5	-48.2	-39.6	-31.7	-35.9	-55.3	405	15.1	1.4	8.6	-4.2
23.07.2000	SG		0	15	23	68	21	W4M	854987	1963	129	37	24	7	-67.6	-48.8	-39.7	-31.8	-34.1	-50.4	397	15.2	1.5	9.2	-2.3
01.08.2000	SCV	4c12	0	12	11	48	23	W3M	872235	3072	381	164	35		-64.6	-40.9	-34.6	-30.8	-34.5		239	8.1	4.7	6.2	-3.8
01.08.2000	SG	4c12	0	12	11	48	23	W3M	120637	450	63	31	8	8	-62.0	-40.5	-36.7	-35.5		-21.4	219	7.1	4.0	3.8	
17.07.2003	SCV	a11		11	20	48	19	W3M	401194	753	67	21	5	13	-70.8	-45.7	-42.1	-34.3	-37.4	-45.7	474	11.3	4.1	3.6	-3.2
12.08.2000	SCV	a11	0	11	20	48	19	W3M	672219	1206	129	87	10	36	-69.0	-44.8	-39.9	-34.4			469	9.3	8.7	5.0	
12.09.2000	SG	a11	[illegible]	11	20	48	19	W3M	59900	125	20	13	16	1040	-66.1	-41.2				-29.2	343	6.1	0.8		
18.12.2003	SCV	a13		13	[illegible]	48	19	W3M	628748	1381	129	34	12	5	-69.1	-43.0	-38.0	-30.5	-30.2		404	10.7	2.8	5.0	0.3
22.09.2000	SG	a13	0	13	19	[illegible]	26	W3M	40941	116	10	3	1		-55.2	-40.7	-42.6	-29.2		-29.9	317	11.5	2.6	-1.8	
17.07.2003	SG	a13		13	19	48	[illegible]	W3M	177552	437	47	14	5	2	-64.7	-41.8	-37.6	-25.5	-20.4	-29.2	353	9.2	2.7	4.2	5.1
18.09.2003	SG	a13		13	19	48	[illegible]	W3M	663627	1629	184	52	26		-64.7	-41.8	-37.6	-25.5	-20.4	-29.2	351	8.9	2.0	4.2	5.1

Table 3-2. Concentrations (ppmv), $\delta^{13}C$ compositions (‰, VPDB) and ratios of hydrocarbon and CO_2 gases from SCV and SG samples collected at the same well site (cont.)

Date	Type	Well LSD							C_1	C_2	C_3	iC_4	nC_4	C_{5+}	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$	$C_1/(\Sigma C_2+)$	C_2/C_3	iC_4/nC_4	ΔC_2-C_3	ΔiC_4-nC_4
GROUP III																									
Summer																									
16.11.1999	SCV		0	14	28	31	23	W3M	891911	6086	2149	2136	707		-56.6	-34.8	-28.0	-31.0	-29.0	-9.7	81	2.8	3.0	6.8	2.0
18.08.2000	SG		0	14	28	31	23	W3M	2717	28	15	23	12		-50.0	-35.3	-27.3	-30.0	-29.0	-29.7	35	1.9	1.9	8.1	1.0
30.08.2000	SCV	a1	0	1	9	52	4	W4M	468026	1179	130	27	11		-62.3	-48.7	-41.1	-32.8	-34.7	-22.6	348	9.1	2.5	7.6	-1.9
30.08.2000	SG	a1	0	1	9	52	4	W4M	4147	14	2	0	0		-43.6	-33.8	-32.4			-17.5	255	7.2	1.2	1.4	
	SCV	4d13	0	13	11	48	23	W3M	901361	3292	436	198	44		-62.6	-40.1	-33.4	-29.7	-34.0		227	7.5	4.5	6.7	-4.2
31.08.2000	SG	4d13	0	13	11	48	23	W3M	136184	389	57	26	4		-56.2	-40.6	-32.2	-29.6		-49.2	286	6.8	6.2	8.4	
11.09.1999	SCV		0	7	11	47	5	W4M	978305	3795	357	69	30		-64.5	-48.1	-41.2	-33.0	-38.0		230	10.6	2.3	6.9	-5.0
11.09.1999	SG		0	7	11	47	5	W4M	54913	120	11	3	1	1	-61.2	-46.6	-40.6	-32.1		-64.2	403	10.6	2.8	6.0	
14.09.2000	SCV	c4	0	4	16	49	26	W3M	772802	2618	263	98	24		-60.4	-41.1	-36.6	-33.4	-34.5		257	10.0	4.0	4.6	-1.1
14.09.2000	SG	c4	0	4	16	49	26	W3M	17992	52	4	0	0		-56.0	-40.0	-36.7			-34.3	317	12.1	1.8	3.3	
14.09.2004	SCV			1	18	48	19	W3M	889308	1598	179	47	15		-69.5	-46.1	-38.8	-38.4			484	8.9	3.2	7.3	
14.09.2004	SG-13			1	18	48	19	W3M	211140	323	38	12	3	2	-62.3	-46.3	-40.7	-33.3		-37.9	561	8.6	3.7	5.6	
	SCV	d11		11	19	48	20	W3M	446971	830	80	49	6		-70.0	-49.0	-41.0	-32.6	-36.8	-19.6	463	10.3	8.8	8.0	-4.3
22.09.2000	SG	d11	0	11	19	48	20	W3M	256081	615	71	52	6	10	-59.5	-46.3	-39.7	-29.4	-29.2	-32.4	345	8.7	8.5	6.7	0.2
26.09.2000	SCV	a14	0	14	23	55	6	W4M	472355	1031	91	48	8		-63.5	-50.7	-41.9	-33.2	-36.9	-13.1	401	11.4	5.9	8.8	-3.7
26.09.2000	SG	a14	0	14	23	55	6	W4M	4767	44	11	9	3	106	-36.8	-44.6	-37.8	-31.5	-33.2	-28.1	71	3.9	3.3	6.8	-1.7
28.09.1999	SCV		0	15	30	47	21	W3M	927619	2365	245	42	22		-64.2	-45.3	-36.4	-30.1	-30.2	-15.3	347	9.6	1.9	9.0	-0.2
28.09.1999	SG		0	15	30	47	21	W3M	41481	82	7	2	2		-60.0	-42.8	-35.1	-28.2		-54.0	446	11.8	1.2	7.7	
Winter																									
17.10.1999	SCV		0	13	20	47	26	W3M	351267	1598	224	37	17		-62.7	-38.8	-31.8	-29.2	-29.0	-8.0	187	7.1	2.2	7.0	0.2
17.10.1999	SG		0	13	20	47	26	W3M	11308	55	3	2	1	3	-58.8	-37.1	-32.5	-26.8		-21.5	188	17.4	1.8	4.6	
	SCV		0	11	20	47	26	W3M	975325	5468	800	124	57		-61.7	-38.4	-31.2	-28.8	-28.6		151	6.8	2.2	7.2	0.2
17.10.1999	SG		0	11	20	47	26	W3M	32823	168	24	5	2	1	-56.6	-36.2	-29.1	-29.3	-26.7	-20.0	165	7.0	1.9	7.2	2.6
	SCV	5c	0	7	3	46	23	W3M	941141	2620	255	49	22		-63.6	-49.3	-39.7	-32.7	-37.7		319	10.3	2.2	9.6	-4.9
17.11.2000	SG	5c	0	7	3	46	23	W3M	100202	196	24	4	1		-56.4	-46.6	-38.6	-31.4	-35.4	-19.2	444	8.3	3.0	8.0	-4.0
19.09.1999	SCV	2D13	0	13	11	48	23	W3M	978195	4210	491	77	36		-64.8	-41.1	-34.2	-28.0	-29.3		203	8.6	2.1	6.9	-1.3
02.11.2001	SG	2D13	0	13	11	48	23	W3M	653369	1820	163	32	12		-60.7	-38.4	-31.1			-46.6	322	11.2	2.6	7.3	
02.11.2001	SG	2D13	0	13	11	48	23	W3M	19956	9	0	0	0		-53.5					-58.7	2184	23.1	1.6		
18.04.2004	SCV			6	19	23	21	w4-0	987000	4000	1000	100			-54.3	-43.5	-31.5	-27.0	-29.7		194	4.0		12.0	-2.7
18.04.2004	SG			6	19	23	21	w4-0	254400	1000	100				-42.9	-41.5				-22.6	231	10.0			
2001	SCV	A15		15	22	49	22	W3M	977633	2486	174	39	11		-68.3	-43.7	-41.2	-34.1	-37.5	-29.7	361	14.3	3.6	2.4	-3.3
15.05.2002	SG	a		15	22	49	22	W3M	225349	617	50	17	4	4	-57.7	-39.2	-37.8	-31.6		-39.0	328	12.3	3.9	1.4	
16.05.2002	SCV	a		2	27	49	22	W3M	270147	654	45	10	2		-70.0	-44.0	-40.6	-31.9	-33.1	-14.4	380	14.6	3.9	3.4	-1.2
16.05.2002	SG	a		2	27	49	22	W3M	175877	211	8	4	0	11	-51.9	-37.4	-37.1	-28.4	-24.0	-50.5	787	26.5	12.7	0.3	4.5
16.05.2005	SCV			8	28	49	22	W3M	996945	2811	197	57	15	17	-67.5	-42.0	-40.3	-33.2	-37.1	-16.0	324	14.3	3.9	1.7	-3.9
16.05.2005	SG			8	28	49	22	W3M	12395	44	2	1	0	8	-51.7	-32.1				-25.9	266	21.3	11.3		

Table 3-3. Temperature measurements (^{o}C) in soil near the wells and in the background

Date	Day	Site	100 cm	170 cm
31.10.02	304	Background	6.1	7.3
24.11.02	328	"	2.6	4.8
17.12.02	351	"	1.2	3.4
04.03.03	425	"	-1.7	-0.6
27.03.03	451	"	-0.5	-0.5
06.06.03	486	"	13.1	10.5
19.06.03	535	"	15.9	11.9
05.08.03	582	"	16.2	13.4
28.08.03	605	"	17.3	15.7
12.09.03	620	"	13.7	14.3
18.09.03	626	"	12.2	12.6
27.09.03	635	Background	11.1	11.6
"	635	A3	12	12.2
"	635	A4	10.6	10.7
02.10.03	640	Background	10.5	11
"	640	A3	10	11.2
"	640	A4	9.3	9.9
16.10.03	654	Background	9.3	9.9
"	654	A3	8.9	10.6
"	654	A4	8.3	n.m.
25.10.03	663	Background	8.7	8.9
"	663	A3	7.9	9.7
"	663	A4	7.6	n.m.
"	663	A10	11	11.5
08.11.2003	677	Background	4.5	8.7
"	677	A3	2	n.m.
"	677	A4	4.1	n.m.
"	677	A10	6.2	8.2
26.11.03	695	Background	2.1	4.5
"	695	A3	0.2	5.4
"	695	A4	1.9	4.1
"	695	A10	3.7	5.5
22.12.03	722	Background	0.5	2.3
"	722	A3	0	4.2
"	722	A4	n.m.	2.1
"	722	A10	1.5	3
07.02.04	768	Background	-0.5	0.8
"	768	A3	-3.9	1.5
"	768	A4	n.m.	0.6
"	768	A10	0.5	2.4
16.04.04	867	Background	n.m.	1.2

Table 3-4. Soil moisture and density measurements (all methods)

Location	A3 (0.3 m)			A3 (1.0 m)			A3 (1.0 m)			A3 (1.0 m)		
Date	25.10.01			27.09.03			25.10.2003			26.11.03		
z (cm)	θ vol. %			θ vol. %	ρ (g/cm³)	n_e	θ vol. %	ρ (g/cm3)	n_e	θ vol. %	ρ (g/cm³)	n_e
-0.1				8.5	1.6	0.40	15.1	1.4	0.47	19.9	1.4	0.45
-0.2	10.0			9.4	1.5	0.43	11.5	1.3	0.51	16.5	1.3	0.50
-0.3				4.4	1.3	0.53	8.5	1.3	0.51	15.1	1.2	0.55
-0.4				2.6	1.3	0.51	7.0	1.1	0.58	12.9	1.3	0.52
-0.5	10.4			1.0	1.2	0.53	9.8	1.3	0.52	14.0	1.3	0.53
-0.6				1.2	1.3	0.50	10.3	1.3	0.50	12.9	1.3	0.52
-0.7				2.3	1.5	0.45	9.8	1.3	0.51	14.4	1.2	0.55
-0.8				3.3	1.4	0.46	9.2	1.3	0.52	16.4	1.2	0.56
-0.9				5.9	1.3	0.49	10.7	1.3	0.50	16.7	1.3	0.53
-1	13.9			4.6	1.4	0.49	8.2	1.2	0.53	14.5	1.3	0.53
-1.1				2.1	1.5	0.45	8.8	1.3	0.52	13.8	1.2	0.54
-1.2				3.1	1.4	0.46	8.9	1.3	0.50	14.4	1.3	0.49
-1.3				4.7	1.5	0.44	10.8	1.3	0.50	14.6	1.3	0.50
-1.4				4.8	1.5	0.44	12.2	1.3	0.51	18.0	1.3	0.52
-1.5	11.9			7.7	1.4	0.48	17.3	1.4	0.49	20.3	1.4	0.47
-1.6				13.2	1.5	0.44	22.5	1.2	0.54	25.1	1.3	0.49
-1.7				19.3	1.4	0.46	30.7	1.4	0.48	32.2	1.4	0.48
-1.8				25.7	1.5	0.45	35.8	1.3	0.51	41.0	1.3	0.51
-1.9				30.1	1.4	0.47	35.6	1.3	0.51	40.6	1.3	0.52
-2				29.8	1.4	0.49	38.7	1.2	0.54	37.3	1.2	0.56
-2.1				31.9	1.2	0.54	37.9	1.4	0.48	39.8	1.4	0.48
-2.2				30.8	1.4	0.45	40.3	1.3	0.52	43.7	1.3	0.51
-2.3				32.1	1.3	0.50	39.4	1.3	0.51	40.0	1.3	0.52
-2.4				32.3	1.4	0.48	39.3	1.3	0.50	48.1	1.3	0.50
-2.45				34.0	1.2	0.55						

Location	A3 (0.3 m)			A3 (1.0 m)			A3 (1.0 m)			A3 (1.0 m)		
Date	25.10.01	25.10.01	25.10.01	27.09.03			25.10.2003			26.11.03		
z (cm)	θ vol. %	θ vol. %	θ vol. %	θ vol. %	ρ (g/cm³)	n_e	θ vol. %	ρ (g/cm³)	n_e	θ vol. %	ρ (g/cm³)	n_e
0								1.6	0.41	0.9	1.7	0.34
-0.15	9.9	8.6			1.6	0.38	1.6	1.6	0.40	5.5	1.6	0.41
-0.25				3.7	1.5	0.44	6.6	1.5	0.44	4.8	1.5	0.44
-0.35				3.9	1.6	0.38	8.2	1.5	0.43	4.0	1.6	0.40
-0.45			6.5	3.3	1.4	0.47	7.5	1.4	0.48	2.2	1.3	0.50
-0.55				2.6	1.5	0.44	7.9	1.4	0.45	1.9	1.5	0.45
-0.65				1.8	1.5	0.45	7.8	1.3	0.50	2.3	1.5	0.44
-0.75				4.3	1.4	0.47	6.5	1.3	0.50	0.4	1.4	0.47
-0.85				4.0	1.4	0.48	7.0	1.2	0.54	0.3	1.4	0.47
-0.95	8.9	9.7	7.5	3.9	1.4	0.49	6.6	1.3	0.51	0.8	1.4	0.46
-1.05				0.8	1.3	0.50	4.7	1.4	0.48	0.0	1.3	0.50
-1.15				3.0	1.4	0.49	6.0	1.3	0.52	0.0	1.5	0.45
-1.25				5.0	1.4	0.46	6.6	1.3	0.49	0.0	1.5	0.43
-1.35				7.0	1.3	0.49	9.9	1.4	0.47	0.0	1.4	0.48
-1.45			11.1	10.5	1.4	0.48	12.9	1.3	0.51	2.8	1.4	0.47
-1.55				11.4	1.4	0.47	14.7	1.3	0.52	5.1	1.4	0.48
-1.65				19.7	1.4	0.47	20.2	1.3	0.52	6.9	1.3	0.50
-1.75				25.7	1.4	0.46	28.6	1.4	0.47	9.8	1.5	0.45
-1.85				31.4	1.4	0.49	35.1	1.4	0.48	18.7	1.5	0.44
-1.95		24.2	23.8	30.8	1.4	0.45	38.5	1.4	0.47	27.4	1.5	0.45
-2.05				33.5	1.3	0.49	39.6	1.4	0.48	29.4	1.4	0.48
-2.15				35.3	1.4	0.48	40.5	1.3	0.53	35.3	1.4	0.46

Table 3-4. Soil moisture and density measurements (all methods)

(cont.)

Location	A3 (2.0 m)	A3 (4.0 m)	Bkgrnd	A3 (4.0 m)			A3 (4.0 m)			A3 (4.0 m)		
Date	25.10.01	25.10.01	25.10.01	27.09.03			25.10.2003			26.11.03		
z (cm)	θ vol. %	θ vol. %	θ vol. %	θ vol. %	ρ (g/cm^3)	n_e	θ vol. %	ρ (g/cm^3)	n_e	θ vol. %	ρ (g/cm^3)	n_e
-2.25				34.3	1.4	0.49	40.6	1.4	0.48	32.6	1.4	0.46
-2.35				32.5	1.4	0.46	39.8	1.4	0.47	34.0	1.4	0.46
-2.4				38.5	1.4	0.49	39.9	1.4	0.46	36.2	1.4	0.46

Location	A4 (0.3 m)	A4 (1.0 m)		A4 (1.0 m)			A4 (1.0 m)			A4 (1.0 m)		
Date	18.06.2002	18.06.2002		27.09.03			25.10.2003			26.11.03		
z (cm)	θ vol. %			θ vol. %	ρ (g/cm^3)	n_e	θ vol. %	ρ (g/cm^3)	n_e	θ vol. %	ρ (g/cm^3)	n_e
0							-10.4	1.0	0.62	-5.8	1.2	0.56
-0.05							5.9	1.6	0.41	12.8	1.4	0.48
-0.15	4.8			19.2	0.9	0.66	14.7	0.9	0.66	19.1	0.9	0.65
-0.25				22.5	1.1	0.60	21.0	1.0	0.61	25.4	1.0	0.63
-0.35				23.8	1.1	0.57	23.7	1.2	0.53	28.2	1.1	0.58
-0.45	19.1	9.1		26.4	1.2	0.56	23.7	1.3	0.50	26.3	1.3	0.52
-0.55				27.1	1.4	0.49	27.2	1.3	0.51	26.7	1.3	0.50
-0.65	19.5			27.4	1.2	0.56	27.5	1.2	0.56	25.1	1.2	0.56
-0.75				30.7	1.2	0.55	27.9	1.2	0.56	28.5	1.2	0.54
-0.85				29.9	1.1	0.59	32.5	1.3	0.53	30.0	1.3	0.52
-0.95	18.4	20.0		33.8	1.0	0.60	34.6	1.2	0.55	34.6	1.2	0.53
-1.05				32.0	1.2	0.56	34.0	1.2	0.55	35.6	1.2	0.56
-1.15				34.2	1.3	0.50	35.4	1.3	0.52	36.6	1.3	0.52
-1.25				38.5	1.0	0.62	38.8	1.0	0.63	39.6	1.3	0.52
-1.35				36.2	1.3	0.52	39.8	1.1	0.57	38.9	1.3	0.51
-1.45	31.8			37.8	1.3	0.51	39.8	1.2	0.55	37.7	1.4	0.48
-1.55				39.1	1.3	0.49	38.8	1.2	0.53	39.4	1.3	0.50
-1.65				38.4	1.4	0.48	38.5	1.3	0.50	39.0	1.4	0.47
-1.75				34.4	1.4	0.46	36.4	1.4	0.46	35.4	1.5	0.45
-1.85				34.0	1.4	0.47	37.1	1.3	0.50	35.5	1.4	0.45
-1.95		32.2		34.8	1.5	0.45	36.4	1.4	0.49	35.1	1.4	0.48
-2.05				36.1	1.3	0.50	32.9	1.4	0.47	36.5	1.3	0.50
-2.1				37.3	1.3	0.51	35.5	1.4	0.45	36.5	1.3	0.51

Location	A4 (2.0 m)	A4 (4.0 m)		Date			Date			Date		
Date				27.09.03			25.10.2003			26.11.03		
z (cm)	18.06.2002	18.06.2002		θ vol. %	ρ (g/cm^3)	n_e	θ vol. %	ρ (g/cm^3)	n_e	θ vol. %	ρ (g/cm^3)	n_e
-0.05							-4.7	1.8	0.3	3.3	1.6	0.4
-0.15	3.0			11.7	1.4	0.5	7.5	1.4	0.5	11.6	1.4	0.5
-0.25				13.7	1.4	0.5	15.1	1.3	0.5	15.7	1.3	0.5
-0.35				10.0	1.3	0.5	10.6	1.4	0.5	11.4	1.3	0.5
-0.45	3.7	10.6		9.2	1.2	0.5	7.7	1.3	0.5	9.1	1.2	0.5
-0.55				8.8	1.3	0.5	10.0	1.3	0.5	10.3	1.4	0.5
-0.65				12.7	1.2	0.5	10.2	1.4	0.5	13.0	1.4	0.5
-0.75				16.2	1.3	0.5	14.9	1.3	0.5	13.4	1.4	0.5
-0.85				16.3	1.3	0.5	16.6	1.4	0.5	17.1	1.5	0.4
-0.95	16.7	18.0		21.3	1.4	0.5	22.2	1.4	0.5	19.6	1.3	0.5
-1.05				24.9	1.4	0.5	25.0	1.3	0.5	23.4	1.4	0.5
-1.15				29.4	1.4	0.5	27.7	1.4	0.5	28.8	1.4	0.5
-1.25				33.6	1.3	0.5	32.8	1.2	0.5	33.3	1.2	0.5
-1.35				34.4	1.2	0.5	36.5	1.4	0.5	35.4	1.4	0.5
-1.45		19.0		35.9	1.4	0.5	36.7	1.4	0.5	36.0	1.4	0.5
-1.55				33.3	1.4	0.5	35.8	1.3	0.5	34.9	1.4	0.5

Table 3-4. Soil moisture and density measurements (all methods)

(cont.)

Location	A4 (200 cm)	A4 (400 cm)	Date			Date			Date		
Date			27.09.03			25.10.2003			26.11.03		
z (cm)	18.06.2002	18.06.2002	θ vol. %	ρ (g/cm³)	n_e	θ vol. %	ρ (g/cm³)	n_e	θ vol. %	ρ (g/cm³)	n_e
-1.65			35.6	1.3	0.5	36.2	1.3	0.5	35.6	1.4	0.5
-1.75			36.7	1.4	0.5	34.7	1.4	0.5	34.6	1.3	0.5
-1.85			34.4	1.4	0.5	36.3	1.4	0.5	32.5	1.4	0.5
-1.95		22.2	34.4	1.4	0.5	36.3	1.4	0.5	34.9	1.4	0.5
-2.05			34.9	1.4	0.5	34.1	1.4	0.5	38.2	1.4	0.5
-2.1			35.0	1.3	0.5	34.6	1.5	0.4	35.6	1.4	0.5

Table 3-5 Average isotope compositions (‰, VPDB) of leaking gases from the three proximal probes.

	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$
A3					
Mean	-68.1	-41.7	-36.8	-31.4	-34.8
Standard Deviation	0.8	0.6	0.6	0.6	1.1
A4					
Mean	-69.0	-46.8	-40.4	-33.7	-37.4
Standard Deviation	0.4	2.9	0.4	0.5	1.0
A10					
Mean	-65.3	-41.5	-35.3	-30.8	-35.2
Standard Deviation	0.7	0.2	0.5	1.6	0.7

Table 3-6 Anion compositions of soil water (mg/l) from soil samples collected near wells A3 and A4 at Edam. Data were corrected using soil moisture content of the respective samples.

	A1	A1-150	A1-150*	B1	B1*	B2	A3	B3	A11-50	A11-100	A14	B14
Chloride	32.9	45.2	n.d.	11.9	19.6	24.1	15.1	93.1	n.d.	n.d.	n.d.	n.d.
Flouride	5.6	9.1	n.d.	n.d.	n.d.	n.d.	0.4	0.6	1.2	3.8	1.3	0.7
Bromide	n.d.	n.d.	0.8	n.d.	0.0	6.0	n.d.	0.3	n.d.	n.d.	n.d.	n.d.
Nitrite	10.2	1.8	351.1	1.5	1.9	3.8	2.3	2.2	7.4	1.1	1.0	0.4
Nitrate	16.5	5.6	n.d.	n.d.	n.d.	n.d.	184.4	20.7	3.3	0.7	2.3	1.2
Phosphate	n.d.	4.1	n.d.	n.d.	n.d.	n.d.	n.d.	1.0	n.d.	n.d.	n.d.	n.d.
Sulphate	51.4	474.9	n.d.	10.8	7.5	10.2	81.4	103.7	490.8	29.5	19.2	9.8

* The samples with an asterisk are collected at the same depth and distance from the well but ca. four years from the initial sampling.

Chapter 4

Morphology and origin of authigenic calcite in soils near the leaking wells

Introduction

Bacterially mediated precipitation of calcium carbonate is a widespread phenomenon (Boquet *et al.*, 1973). Microorganisms are associated with carbonate precipitation in marine, saline lake, soil, and "deep" sediment environments (Hammes and Verstraete, 2002). Kidney stone formation and the precipitation of carbonate in the Martian meteorite ALH84001 are also attributed to microorganisms (Hammes and Verstraete, 2002). Two major mechanisms of bacterially mediated carbonate precipitation are proposed: active and passive (Castanier *et al.*, 1999). Active carbonatogenesis is a poorly understood process that involves ionic transport through the cell membranes of the microorganisms. Examples of microorganisms that employ active precipitation are the photosynthetic algae and cyanobacteria (Hammers and Verstraete, 2002). The best morphological evidence for active carbonate precipitation is growth of calcite crystals within and on top of the microorganisms. This growth eventually leads to the death of the microorganisms followed by a complete replacement by carbonate (Castanier *et al.*, 1999). Carbonate precipitation on cell surfaces and in the microenvironments surrounding the cells is also attributed to the ability of bacteria and polysaccharide film to provide nucleation sites (Merz-Preiss *et al.*, 1999; Warren *et al.*, 2001).

During passive carbonate precipitation bacteria participate in the mineral forming process by modifying the chemical composition of the local environment. The metabolic activities of bacteria lead to the accumulation of bicarbonate ion and a concomitant rise of the alkalinity and/or pH of the milieu. Passive precipitation is a by-product of several metabolic pathways: amino-acids ammonification; urea and uric acid degradation; and dissimilatory nitrate and sulphate reduction (Castanier *et al.*, 1999; McGenity and Selwood, 1999). Autotrophic metabolic pathways, such as non-methylotrophic methanogenesis and cyanobacterial photosynthesis, are also involved in carbonate precipitation, however, heterotrophic carbonatogenesis is much more prevalent in marine environment (Castanier *et al.*, 1999).

A variety of mineral textures reflect the involvement of microorganisms in carbonate precipitation. These are spheroid, rod, filamentous and vibrioid textures indicative of direct cellular replacement, as well as ooid, fibrous, and dumbbell shapes attributed to a combination of biogenic or abiogenic processes (Monger *et al.*, 1991; Braissant *et al.*, 2003; Hammes *et al.*, 2003; Henriksen *et al.*, 2002). Other textures have less to do with the direct involvement of microorganisms in mineral precipitation and have been attributed to supersaturation (e.g., crusts, radial aggregates) or microgradients in the medium (e.g., dendritic textures).

This chapter focuses on the morphology of soil calcite samples collected near the leaking wells. The principal goal of this chapter is to study the role microorganisms play in immobilizing natural gas and oil derived carbon in soil near the leaking wells. Results of this chapter are also intended to help better understand the factors that may have an impact on the stable isotope compositions of bulk and selected carbonate samples collected at the leaking well sites (Chapter 6). The composition and morphology of authigenic calcite samples is examined with high resolution Scanning Electron Microscope (SEM) imaging with Energy Dispersive X-Ray (EDX), and X-Ray diffraction analyses. SEM imaging is used to classify the different types of authigenic calcite.

Results

Authigenic minerals in soil near the leaking wells

The most abundant authigenic mineral in soils near the leaking wells is calcite. XRD and EDX spectra demonstrate that both pure calcite and Mg-calcite are present in the samples (Figures 4-1, 4-2). SEM imaging and EDX analysis of selected soil samples also reveal the presence of dolomite in the soil near well A3 (Fig. 4-3a,b). Although clay-sized authigenic dolomite is found in saline soils in Alberta (see Kohut *et al.*, 1995), dolomite is the dominant detrital carbonate in Alberta and Saskatchewan soils (Miller *et al.*, 1987; Landi *et al.*, 2003). The size and rounded morphology of dolomite crystals found near well A3 are similar to those of detrital dolomite from orthic regosoil in Southern Alberta (Miller *et al.*, 1987), suggesting that the former mineral is also of detrital origin.

Authigenic pyrite is also detected by XRD in samples of rust and carbonate scales collected from the casings of two Aberfeldy wells (e.g., A9 and C4). Authigenic pyrite framboids are also observed with SEM in a shallow (0.5 m) soil sample from the active zone of natural gas oxidation at well A3 (Fig. 4-5). Siderite ($FeCO_3$) is detected by XRD in one sample of carbonate/iron hydroxide crust collected from the casing of well A9 at Aberfeldy (Fig. 4-4). Rare halite crystals (NaCl) are also detected by SEM and EDX in a shallow soil (0.5 m) sample collected at well A4. The presence of halite may be the result of natural salinization of the soil or to a leakage of formation water either during well testing and completion or during injection (well A4 was intended to be used as a water injection well; IHS Energy, 2001).

Morphology of authigenic calcite

Authigenic calcite forms crusts that coat the steel casings of wells, mineral grains, lithic clasts, and detrital plant fragments (Fig. 4-6b). In soils authigenic calcite also cements mineral grains and forms aggregates (Fig. 4-6a). Calcite is white to yellow or brown when associated with iron hydroxides. Authigenic calcite aggregates in soils are rare and small (i.e., >2 mm), whereas carbonate crusts along the rusting steel casings of the leaking well bores at Aberfeldy extend for up to several metres. The thickness of the calcite crusts reaches 5 mm.

Authigenic calcite is often found in or close to clay-rich domains in the sandy soil at Edam. Acid tests confirm that these domains contain more carbonate of probable detrital origin rendering the former potential sources of Ca^{2+} - an important limiting factor for authigenic calcite growth. Authigenic calcite also replaces partially or completely small cement fragments common in the soil near the wells, which demonstrates the importance of the latter as an alternative source of Ca^{2+}. Carbonate pendants are also found at the A10 well site. The pendants are common in prairie soils and comprise laminated layers of carbonate coating that form on the lower side of pebble or cobble size lithic clasts in different soil types (Wang and Anderson, 1998; Landi *et al.*, 2003).

SEM imaging reveals that there are two distinctly different types of authigenic calcite. The first type has morphological features typical of inorganic authigenic precipitate (e.g. Monger *et al.*, 1991). The second type exhibits a variety of morphologies, some of which are considered evidence of bacterially mediated precipitation (Monger *et al.*, 1991; Castanier *et al.*, 1991: Warren *et al.*, 2001). This type of calcite is almost invariably associated with bacteria-like objects and with what appears to be microbial film. A review of the textures and morphologies of type I and type II calcite is provided below:

Type I (abiotic) calcite

The first type of authigenic calcite is found predominantly along the casings of the leaking wells at Aberfeldy. Abiotic calcite is also found in the deeper soil horizons close to the well bore of well A3 but it is conspicuously missing from samples collected in the shallow soil near the wells at Edam and also from the upper 0.7-1.0 m along the casings of the Aberfeldy wells. Abiotic calcite forms crusts that consist of equigranular, euhedral crystals of sub-micrometre size (0.3-1.0 μm) that in some instances are associated with larger (3-5 μm across) rhombohedral crystals growing on top of the crusts (Fig. 4-10a, b; 4-11a, b). SEM imaging of rust and carbonate crusts collected at well C4 reveals sparry calcite micro morphologies considered typical for inorganic authigenic calcite precipitation (Fig. 4-11a, b; Monger *et al.*, 1991). Large calcite rhombohedra are not observed in the Aberfeldy samples (Figs. 4-11a, b).

Type II (bacteriogenic) calcite

In contrast to abiotic calcite, the second morphological type of authigenic calcite is found in shallow soils near wells A3 and A4. This type of calcite, however, is missing from samples collected along the well bores of the excavated wells, and also from the deepest parts of the soil around well A3. There authigenic calcite grows in the shape of flat massive crusts and highly porous microcrystalline aggregates (Fig. 4-12a, b, 4-13a). These aggregates form bridges that cement mineral grains or coat the surface of larger grains. A calcite pendant found near well A10 also consists of highly granular calcite of similar size and morphology (Fig. 4-13b).

The massive crusts of authigenic calcite are found predominantly in shallow depressions on the surfaces of the mineral grains. The crusts are discontinuous and contain domains of porous calcite. In contrast to the abiotic calcite, the sizes and morphologies of individual crystalline fragments that build the bacteriogenic calcite aggregates vary widely. A correlation between size and degree of apparent crystallinity is observed in the porous domains/aggregates with many small (i.e., nano-sized) particles of rounded and cauliflower-like, textures (Figs. 4-14a, b). The smallest particles are less than 50 nm across, and appear to coalesce and grow into larger crystals of rough rhombohedral shapes with variable degrees of distortion. The larger crystals build columnar structures that form highly porous maize-like constructions (Figs 4-15a, b). At flat mineral grain surfaces the nm-size particles also coalesce to form massive layered crusts (Fig. 4-16).

As mentioned, type II calcite appears to be almost always associated with bacteria and microbial film-like objects. The only sample where this type of calcite is not associated with bacteria and/or microbial film-like structures is the pendant found at well A10. Evidence of calcite dissolution observed in this sample, however, indicates that this calcite was out of equilibrium with its local environment. Therefore, the prior involvement of bacteria in calcite growth in this sample cannot be precluded (Fig. 4-17a, b).

Evidence for biological origin of the bacteria and microbial film-like structures

Coccoid and rod-shaped bacteria-like objects are observed in a number of soil samples collected at different depths near the well bores at wells A3 and A4. The bacteria-like objects are found in most soil samples near wells A3 and A4, with the highest densities observed in shallow (0.5 m) soil near well A3. SEM imaging also shows that some mineral particles and lithic clasts are covered with polysaccharide-like film (Fig. 4-7a, b). The large diversity of inorganic structures that resemble microorganisms and their by-products precludes the justification of microbial origin judging by shape, and size alone (Hamilton, 2000 and the references therein). However, along with the size, shape and spatial distribution of the bacteria-like objects there are other lines of evidence that those are indeed unicellular microorganisms. The most important one is the rapid desiccation observed when the objects are exposed to electromagnetic emission during SEM imaging. The small spheres and rods change their shape and lose as much as one third of their volume in the matter of seconds (Fig. 4-8a, b). In addition, most bacteria-like objects, in the samples collected at different depths near wells A3 and A4, exhibit evidence of desiccation likely caused by the high vacuum and exposure to electromagnetic emissions during the sputter-coating of the samples.

Soil bacteria are known to produce amorphous slime secretion or capsules of extracellular polymer as means of attachment to mineral surfaces (Hilger *et al.*, 1999). Excessive polysaccharide film production from methanotrophic bacteria is common in landfill cover soils and has been attributed to nutrient imbalance and/or O_2 deficit (Hilger *et al.*, 1999; Hilger *et al.*, 2000). Occurrence of desiccation cracks in the microbial film-like substance observed in the samples collected near the leaking wells is also evidence for biological origin (Fig. 4-9a, b). The cracks indicate loss of volatiles from the natural polymer due to exposure to vacuum and/or electromagnetic emission. Therefore, the observed desiccation phenomenon is strong evidence in favor of biological origin for the observed structures.

Morphology of authigenic pyrite and relationship with bacteria/microbial film

Authigenic pyrite at well A3 is spatially associated with bacteriogenic calcite. Bacteria and microbial film are also seen in this sample. Framboid textures are considered evidence of biological origin. Although inorganic precipitation may also produce framboidal pyrite (Sweeney and Kaplan, 1973), the sulphur stable isotope compositions of most naturally occurring framboids indicate biological origin (Strauss, 1997). Unfortunately, the small amounts and dispersed nature of pyrite in the soil samples precluded the use of stable isotope analysis as a tool to establish the nature of pyrite precipitation.

Morphology of bacteria and microbial film associated with bacteriogenic calcite

There are several morphological types of bacteria observed on the surface or in the porous spaces of the authigenic calcite aggregates. The predominant morphology is coccoid. Cocci comprise between 60 to 70 % of all microorganisms in the samples. The average diameter of the cocci is about 0.5 μm. The small spheres are often seen spread over the mineral surface in a carpet-like cover along with abundant microbial film (Figs. 4-18a, b). Some cocci exhibit medial partitioning typical of microorganisms at the stage of cellular division, suggesting that the bacterial community was active at the time of sampling (Fig. 4-7b).

The second most common morphological type is the rod-shaped bacteria. The rods are straight (Fig. 4-20a) or have vibrio-like shapes (Fig. 4-7a) and are usually much larger then the cocci (i.e., ca. 2 μm long). In samples from well A3 rods comprise as much as 40 % of the bacterial population, although at places their count falls to <10 %. Rods are not found in any of the A4 samples, however. In contrast to coccoid bacteria, rods do not form clusters but are distributed separately. Much smaller, nanometre-size rod-shaped objects are also observed in one sample collected at 1.0

mbs and 0.3 m away from the well bore of well A3. The nano-size rods form colony-like agglomerates (Fig. 4-20b) that bear strong resemblance (in shape, size and distribution) to the carbonate rods found on the surface of altered pyroxene crystals of the Tatouine meteorite from South Tunisia (Benzerara *et al.*, 2003). The origin of the Tatouine rods is attributed to biological activity and the following arguments are used to justify biological origin: rods cluster in ways similar to bacterial colonies, their sizes vary within certain limits consistent with natural variation amongst microorganisms, and minerals do not usually grow in vibrioid shapes (Benzerara *et al.*, 2003). The strong resemblance between the nano-sized rods observed in this study and the Tatouine rods suggests that the former are also of biological origin. In addition to the coccoid and rod (vibrioid) bacteria, long filamentous structures of apparent biological origin (140 nm thick) are also observed in few samples (Fig. 4-9a and 4-21a). On the basis of their morphology, the filaments are likely to be fungi.

As mentioned above, microbial film covers significant part of the mineral surfaces in several samples. The film is estimated to be several tens of nanometres thick and it is often seen bridging columns in the porous authigenic calcite aggregates (Figures 4-9a, b) or serving as an attachment between the bacteria and mineral surfaces (Fig. 4-7b). Microbial film is also seen in a sample collected close to the water table immediately next to the well casing at well A3 (Fig. 4-21b).

Not all samples have the same variety and/or distribution of microorganisms and/or microbial film. The greatest variety is found in samples collected from shallow soil (0.5 m) near the well bore of well A3. The microorganisms found in this sample include cocci, rods, and filamentous objects. In contrast, a sample from the shallow soil near well A4 contains abundant cocci and filaments, but no large rods. It is worth noting that there is no visual and EDS evidence for the association of bacteria in calcite precipitation in the A4 sample, which may indicate that calcite precipitation is a function of the metabolic activity of only one of the bacterial populations, or of the entire consortium working in some form of symbiotic relationship.

A sample collected at 1.0 mbs near well A3 contains only small rods, whereas another sample collected at 2.0 mbs at the same well contains microbial film only. Although bacteria is not found in the latter sample, the presence of microbial film indicates that bacteria exists where natural gas concentrations approach 100 % by volume and oxygen content could be as low as 400 ppm v/v (Chapter 3).

Discussion

Morphological evidence for abiogenic origin of type I calcite

The relatively uniform size and euhedral morphology of calcite crystals from the crusts that precipitate on mineral grains in soils and along the casings of the leaking wells are considered evidence of inorganic precipitation. As mentioned above, the crusts consist of a large number of sparry rhombohedra and/or larger isolated rhombohedra with planar crystalline faces. The planar faces and subdued surface topography of type I calcite crystals suggest mineral growth at low levels of supersaturation or in the presence of specific ions (sulphate, ammonium, divalent metal ions) in the soil solution (Paquette *et al.*, 2002).

Sparry, euhedral morphologies are considered evidence of abiotic precipitation of authigenic calcites in a variety of soils around the world (e.g., Monger *et al.*, 1991; Pal *et al.*, 2000; Kapur *et al.*, 2000; Khokhlova and Kouznetzova, 2004). Fine-grained authigenic dolomite crystals (e.g., 0.5 μm) also exhibit short prismatic to isometric and/or rhombohedral shapes (Kohut *et al.*, 1995). The euhedral morphology of dolomite and siderite rhombohedra found in the gas hydrate bearing sediments on the Blake Ridge is also considered evidence of authigenic origin (Rodriguez *et al.*, 2000). Although euhedral calcite rhombohedra may form as a result of passive microbially mediated precipitation in environments of low medium viscosity and low microbial film content (Braissant *et al.*, 2003), the lack of microorganisms and microbial film in the Edam and Aberfeldy samples supports abiotic origin.

Microbial vs. abiotic origin of type II calcite

The most important indirect evidence for the involvement of the microorganisms in calcite precipitation is the spatial distribution of type II calcite and its intimate association with bacteria and microbial film (cf. Jansen *et al.*, 1999). As mentioned before, optical, SEM investigations, and stable isotope data (Chapter 6) indicate that type II calcite is found only in shallow soils near the leaking wells at Edam. A random search for bacteria and microbial film associated with carbonate minerals of apparent detrital origin in the same samples and in other samples, collected at different depths and distances from the well bores at Edam, returned negative results.

The best evidence for direct involvement of bacteria and/or microbial film with type II calcite formation is the observed precipitation of irregular nano-size particles directly on the surface of the rod-shaped bacteria (Fig. 4-22a, b). These particles are much smaller that the rod and coccoid bacteria, having sizes of <100 nm. The precipitation of nano-size particles on the microbial surfaces is a common phenomenon attributed to modifications in the chemical composition of the microenvironment surrounding the microorganisms (Castanier *et al.*, 1999; Hammes and Verstraete, 2002). It is also hypothesized that carbonate nucleation is facilitated by the attraction between the positively charged Ca and Mg ions and the electronegative walls of the microorganisms (Rivadeneyra *et al.*, 1998). The concentration of metallic ions along the bacterial surfaces triggers nucleation by lowering the supersaturation threshold needed to initiate precipitation (Ferris and Roden, 2000). Growth of small rounded particles of calcite on top of the microbial surfaces is also documented during experiments involving precipitation of calcite mediated by ureolitic bacteria (Warren *et al.*, 2001). Castanier *et al.* (1999) also note that incipient calcite growth on the surfaces of bacteria produces nano-size particles that coalesce to form a thicker rigid coating. Plate-like calcite crystals protruding between individual bacteria in the A3 samples that have high bacterial count and abundant microbial film (Figs. 4-23a, b) are evidence of the formation of such coating. The tiny crusts appear to have grown on top of the bacteria and/or microbial film (Figs. 4-23a, b). The crusts also appear to have been crushed and displaced either by the growing bacteria or by desiccation related to sample preparation and SEM imaging (Fig.4-23 a, b).

Relationship between bacteria, microbial film and the morphology of bacteriogenic calcite

As mentioned above, there are two principal morphological types of bacteriogenic calcite. The first type comprises crust-like accumulations that grow on the surface of detrital mineral grains and lithic clasts (Fig, 4-16). The second morphological type consists of highly porous crystalline aggregates that cement mineral grains and lithic clasts (Figs.4-13a, b). The porous aggregates grow separately, or form domains in the flat crusts. SEM imaging shows that incipient growth of bacteriogenic calcite in both the massive crust and porous aggregate starts with the precipitation of nano-size particles of irregular to rounded (cauliflower, dendrite, coral-like) appearance. Similar evolution from nano-size precipitates of less ordered, amorphous morphology towards larger particles of more "crystalline" shapes has been documented by Castanier *et al.* (1999) during series of *in vitro* experiments that examine bacterially mediated calcite precipitation. Laboratory culture experiments to study calcite precipitation mediated by different strains of ureolitic bacteria also demonstrate that incipient precipitates consist of amorphous calcite that evolves into "more crystalline" structures (Hammes *et al.*, 2003).

A close relationship between the morphology of bacteriogenic calcite and the abundance of bacteria and microbial film is also observed in this study. SEM imaging shows that nano-size particles in the massive crust domains coalesce to form flat, layered step-like structures (Fig. 4-16). In contrast, in the porous domain particles coalesce to form more or less irregular rhombohedra that eventually grow into column-like structures (Fig. 4-15a, b). SEM imaging also demonstrates that the massive crusts are associated with abundant bacteria and thicker, and continuous microbial film. In areas where porous calcite grows, however, bacterial counts are low and microbial film is thinner and discontinuous (Fig. 4-23b).

Braissant *et al.* (2003) report a similar relation between calcite morphology and the amount, viscosity, and relative amino-acid acidity of microbial film and the rates of metabolic activity of bacteria. In their experiments Braissant *et al.* (2003) observe that growth of calcite and vaterite in a medium where the viscosity of the exopolysaccharide film and metabolic activities of the bacterial population are higher produce precipitates of less ordered, dendritic to rounded shapes. In addition, Warren *et al.* (2001) reports that the bacterially mediated precipitation of massive layered carbonate crusts is evidence of high levels of supersaturation. The experiments of Braissant *et al.* (2003) demonstrate that calcite precipitates associated with thin and discontinuous microbial film exhibit higher degree of "crystallinity" and form well defined rhombohedra with planar faces and flat crystal surface morphologies similar to those of calcite crystals grown during abiotic experiments, in a medium where the levels of calcite saturation saturation are low (Paquette *et al.*, 2002).

The observations of this study are consistent with the findings of Warren *et al.* (2001) and Braissant *et al.* (2003). The association of abundant bacteria and thick microbial film with massive carbonate crusts in calcite samples from well A3 indicates that the morphology of calcite in these areas is associated with the abundance of microorganisms and microbial film. Therefore, the massive flat crusts likely form as a result of high levels of supersaturation brought about by the metabolic activity of a larger number of microorganisms, in conjunction with the abundance and, perhaps, the specific chemical composition of the microbial film in these areas. In contrast, the precipitation of more ordered calcite crystals that build the porous calcite structures is related to lower levels of supersaturation due to the low metabolic activity of bacteria (i.e., lesser number of bacteria), lower viscosity of the growing medium, and thinner and discontinuous microbial film of possible different chemical composition.

Soil bacteria and calcite precipitation

A large number of different microorganisms are known to mediate calcite precipitation in laboratory environments (Boquet *et al.*, 1973). Precipitation of authigenic carbonate (calcite and vaterite) by two common types of aerobic soil bacteria: ***Xantobacter autotrophicus*** and ***Ralstonia eutropha*** was observed in laboratory environments (Braissant *et al.*, 2003). However, most of these microorganisms are cultured in media abundant in nutrients not available in soils, at least not in the concentrations applied during the lab experiments (Boquet *et al.* 1973).

Precipitation of calcium carbonate (calcite, Mg-calcite, and aragonite) associated with anaerobic oxidation of methane near CH_4 seeps at the seafloor is considered an inorganic process triggered by supersaturation in local microenvironments near the seeps (Elvert *et al.*, 2000). Others however, suggest that it is directly mediated by the microorganisms from the methanotrophic consortia (Lein *et al.*, 2002; Aloisi *et al.*, 2002). There have been no reports in the literature (at least not to the author's knowledge) that demonstrate a direct association between aerobic methanotrophic bacteria and calcite precipitation. Heterotrophic bacterial communities that mineralize recent organic matter are abundant in the upper 5-10 cm in the soil horizon. In contrast, methanotrophic bacteria that use methane as a sole carbon and energy source are found much deeper in the soil (Kotelnikova, 2002). Although this study provides evidence that bacterial oxidation (aerobic and perhaps anaerobic) of methane proceeds at depths of >1.5 m near the well bore and as deep as 2.0 m away from well bore (Chapter 3), it does not provide information as to the type of bacteria calcite precipitation is associated with.

The variety of morphological types and sizes of the microorganisms observed indicates that they belong to several different strains. The spatial association between large rod-shaped bacteria and calcite precipitates observed in soil samples collected near well A3 suggests a possible genetic relationship. The rod-shaped bacteria resemble the *Pseudomonas* genus that consist of gram negative microorganisms common in soil and groundwater. These are usually obligate aerobes capable of growing on virtually anything that contains carbon (Chapelle, 1993). *Pseudomonas* are common in a variety of soils contaminated with liquid hydrocarbons and actively participate in the mineralization of the contaminants (Chapelle, 1993). In fact, a variety of *Pseudomonas* called *Pseudomonas calcis* was the first bacterium capable of precipitating calcite that has been successfully isolated in laboratory experiments in 1913 (cf. Boquet *et al.*, 1973). Although different strains of aerobic methanotrophic bacteria may have morphologies similar to those described above, in the absence of nucleic acid and/or phospholipids fatty acid (PLFA) analysis data, Fluorescence In-Situ Hybridization (FISH) imaging or the use of polymerase chain reaction (PCR) to amplify and determine the DNA of the microorganisms involved, it is impossible to determine the type of bacteria in the sample (McGentry and Selwood, 1999; Boetius *et al.*, 2000).

Conclusions

Optical, SEM, EDX and XRD investigations reveal the presence of several authigenic minerals in soil samples collected near the leaking wells. These include calcite (normal and Mg-calcite), pyrite, and siderite. Two types of authigenic calcite are found in the soil samples: type I is rarely found in soils near the wells at Edam as well as in scales that precipitate on the surfaces of well bores at Aberfeldy. The morphology of type I calcite suggests inorganic precipitation. Type II authigenic calcite is found only in soil from the active zones of hydrocarbon oxidation. Populations of bacteria of various shape (e.g., rods, cocci) and microbial film are both closely associated with type II authigenic calcite in the soil samples. Mineral growth on the microbial surfaces and evidence of bacterial replacement by calcite reveal the active role of microorganisms with type II calcite precipitation. There is also a strong relationship between the abundance of bacteria and microbial film and the morphology of type II calcite that is consistent with the results of the experimental studies of Braissant *et al.* (2003). The association of pyrite with type II calcite indicates that, at least in some instances, type II calcite precipitation occurs in anoxic environment.

Refe[illegible]

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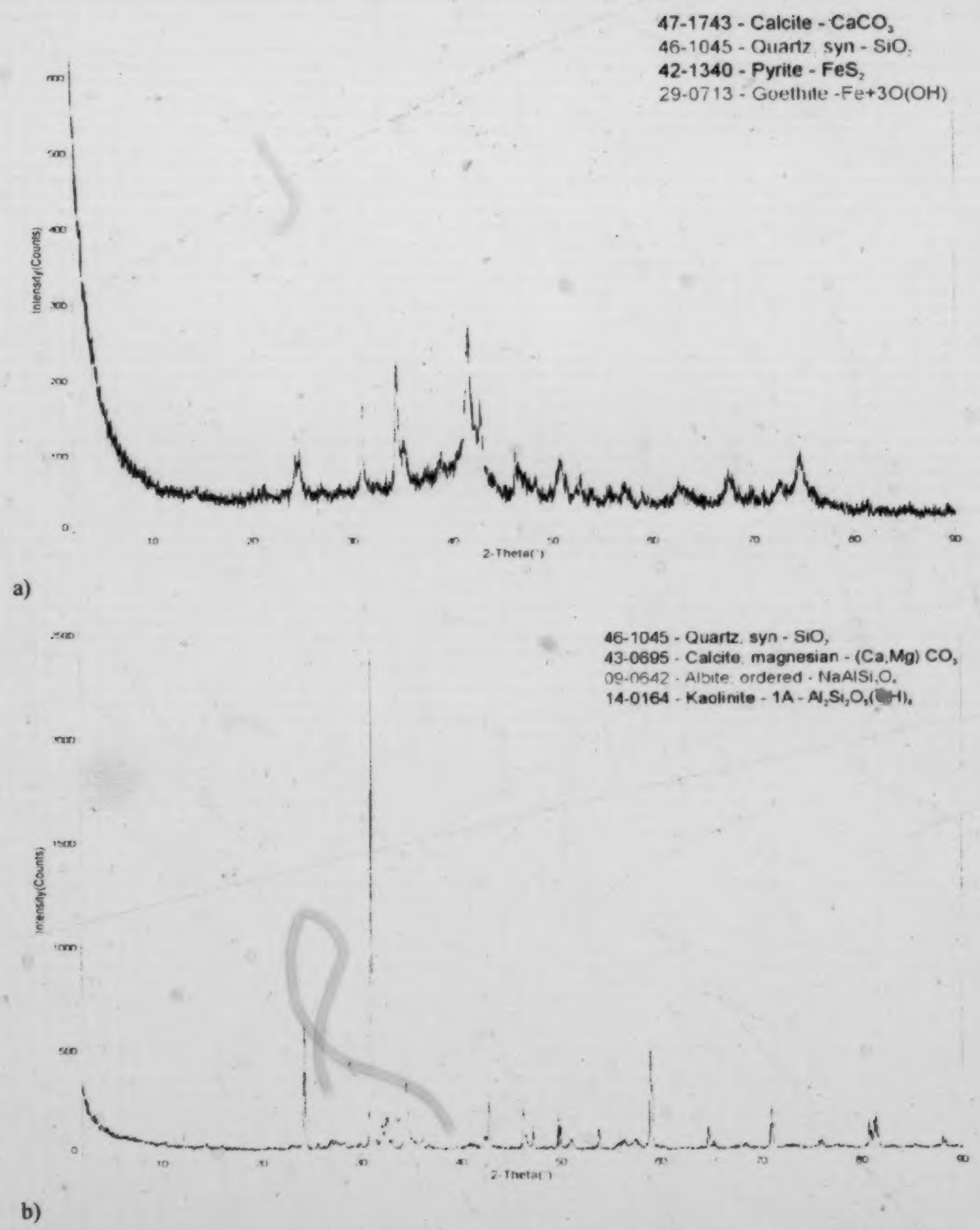


Figure 4-1 (a) XRD spectra of a sample of calcite crust collected from the casing of well C4-15 from the Aberfeldy Oil field, Saskatchewan. Magnesioferrite is also identified in this sample; b) XRD spectra of a sample of calcite crust collected from the casing of well C8-17, same field. Banalsite is also identified in this sample.

X-ray Display 1

Acquisition completed.

1646 FS
B1_150_001
Ca
Ca
Fe
Na
Al
Si
Ir
Cl
K
Fe
Ir
0.0
2.0
4.0
6.0
8.0
10.04
keV

a)

X-ray Display 1

Acquisition completed.

2113 FS
GA8_
Ca
O
Ca
Fe
Al
Si
Ir
K
Fe
Ir
0.0
2.0
4.0
6.0
8.0
10.0
keV

b)

Figure 4-2 (a) EDX spectra of calcite crusts covering mineral grains collected in soil near well A3, Edam and (b) from a pendant collected in the shallow soil near well A10, Maidstone.

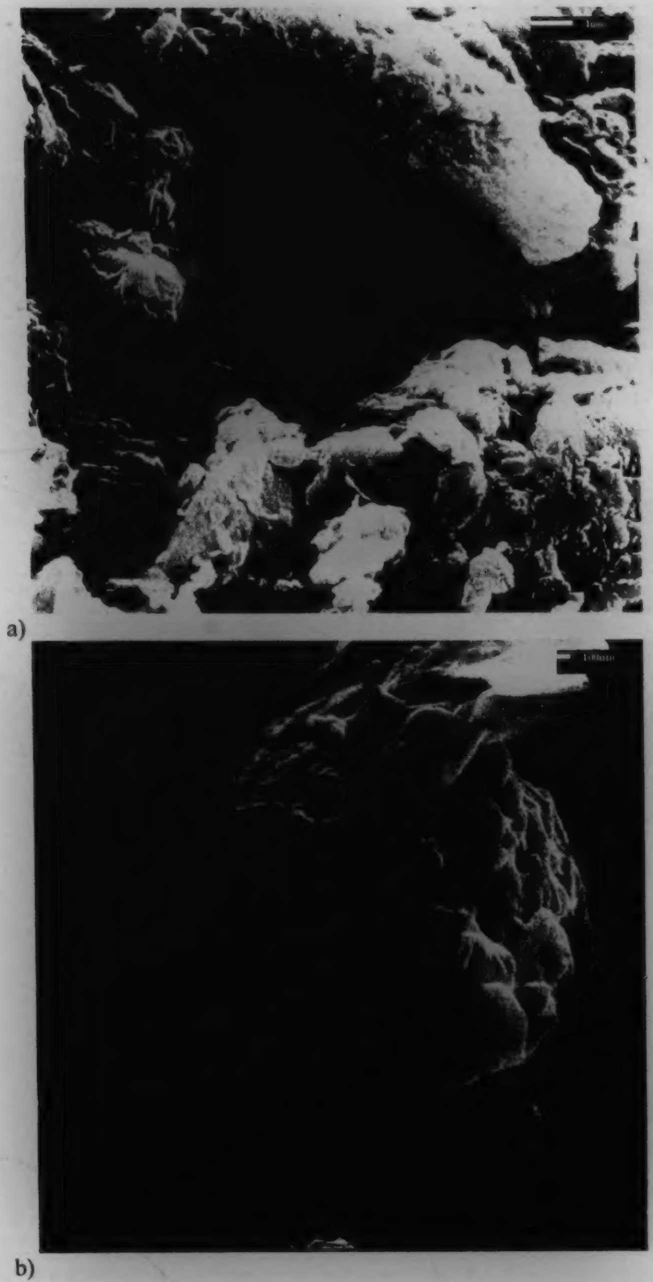


Figure 4-3 (a) Detrital dolomite grain in the soil near well A3. Figure 4-3a shows the surroundings of the grain which consists mostly of clay and other detrital mineral particles. The dolomitic composition of the grain was determined by a semi quantitative EDX analysis. (b) A close-up view of the grain. The rounded shape supports detrital (aeolian) origin.

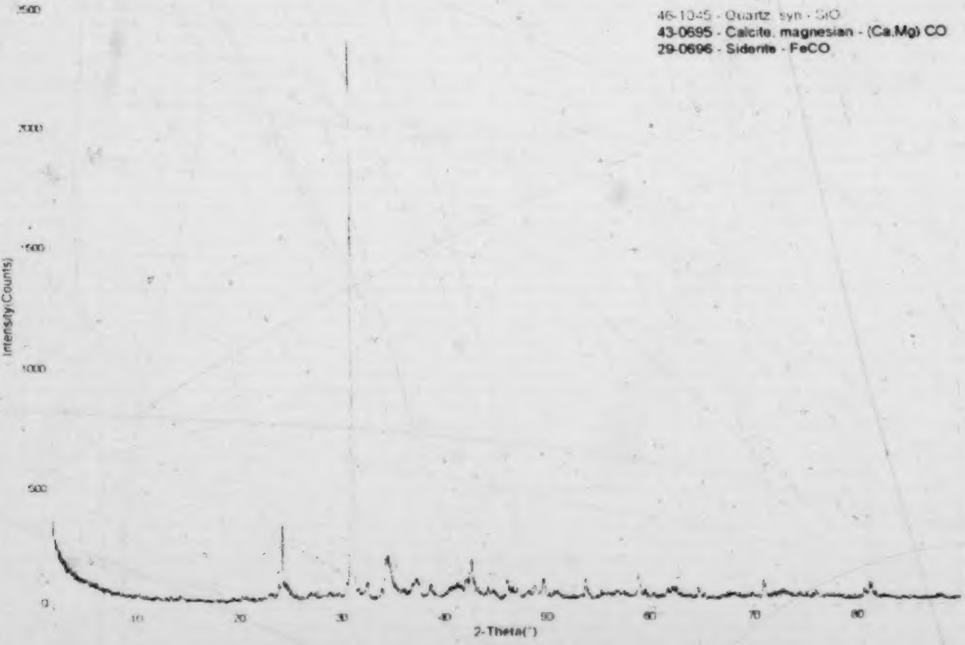


Figure 4-4 XRD spectra of a sample of carbonate/rust scaling collected at 2.47 mbs from the casing of well A9-17, Aberfeldy oil field. Other mineral phases identified in this sample include Magnesioferrite, Goethite and Anorthite.

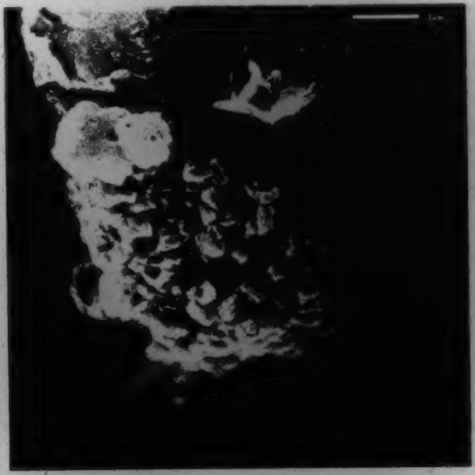


Figure 4-5 Framboid pyrite in close association with authigenic calcite (type II). The sample was collected at 0.5 mbs and 0.3 m away from the well bore of well A3, and provides evidence for the existence of anaerobic conditions in parts of the soil.

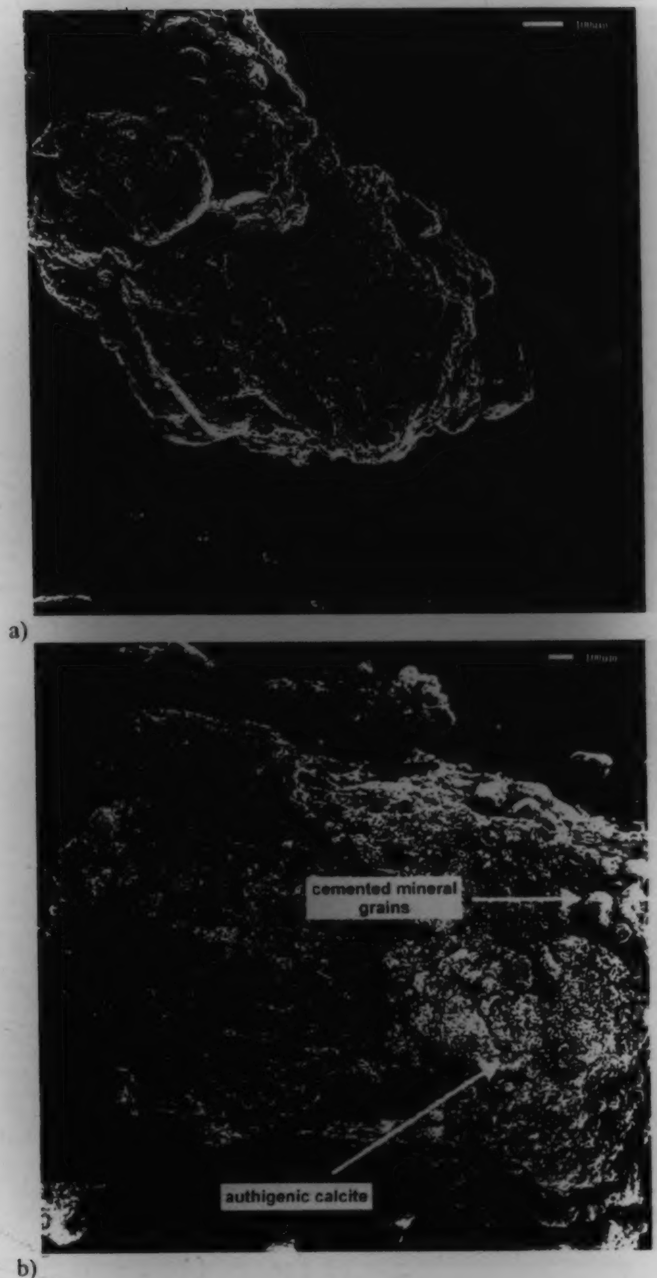

a)
cemented mineral grains
authigenic calcite
b)

Figure 4-6 (a) SEM image of an aggregate that consists of soil mineral grains coated with and cemented by authigenic calcite (0.5 mbs, 0.3 m distance from well bore, well A3, Edam). (b) A rare occurrence of a wood fragment coated with authigenic calcite.

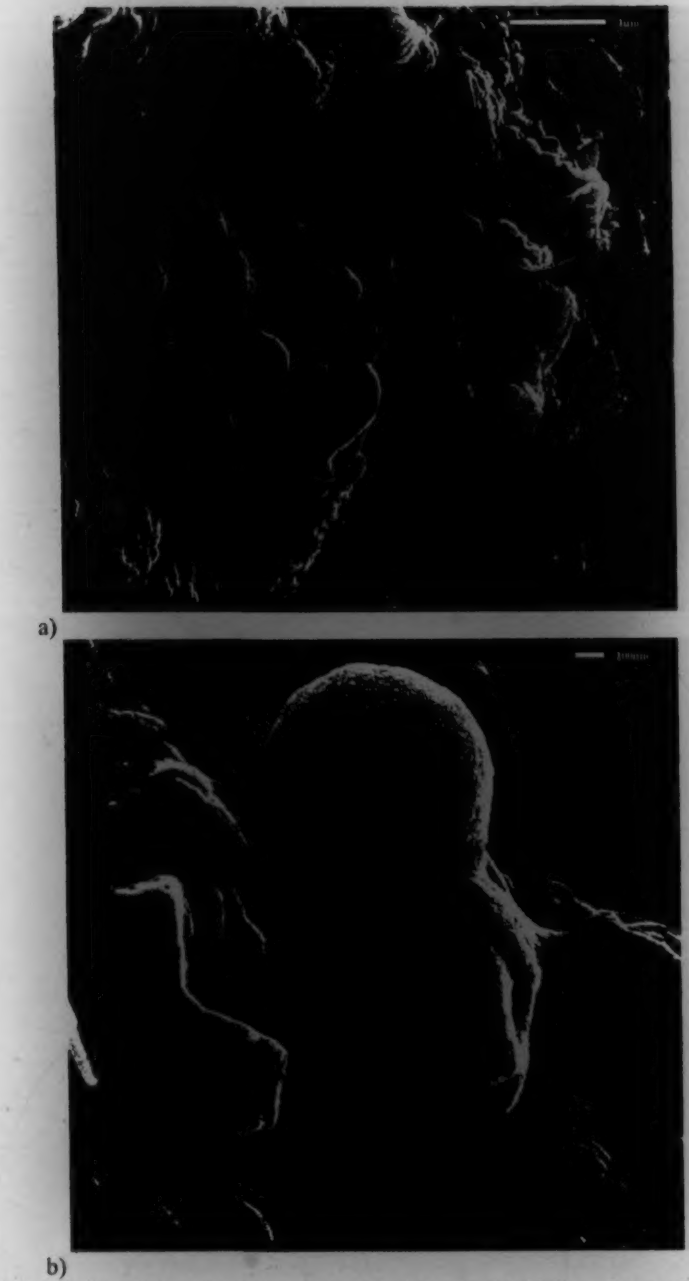


Figure 4-7 Bacteria-like objects in soil samples near A3 well. Rod-like and coccoid shapes are equally common. (a) Considerable amount of desiccation is seen to have affected some rods and also the lower coccoid individual on (b). Clustering of coccoid bacteria-like objects is common. (b) It could be seen that the two coccoid objects are connected to the mineral surface by a microbial film-like substance.

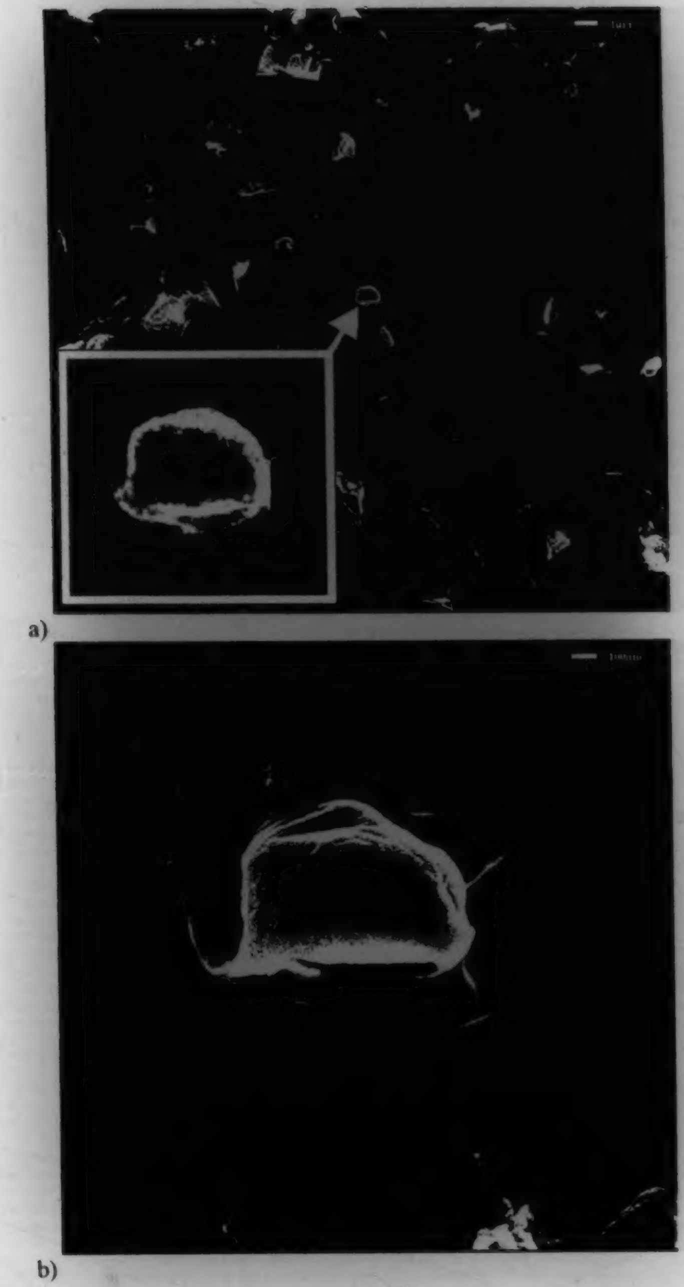


Figure 4-8 (a) Coccoid bacteria-like object at lower magnification was clearly seen to change shape and shrink (b) when higher magnification was applied. The sample was collected from soil at 0.5 mbs near well A3.

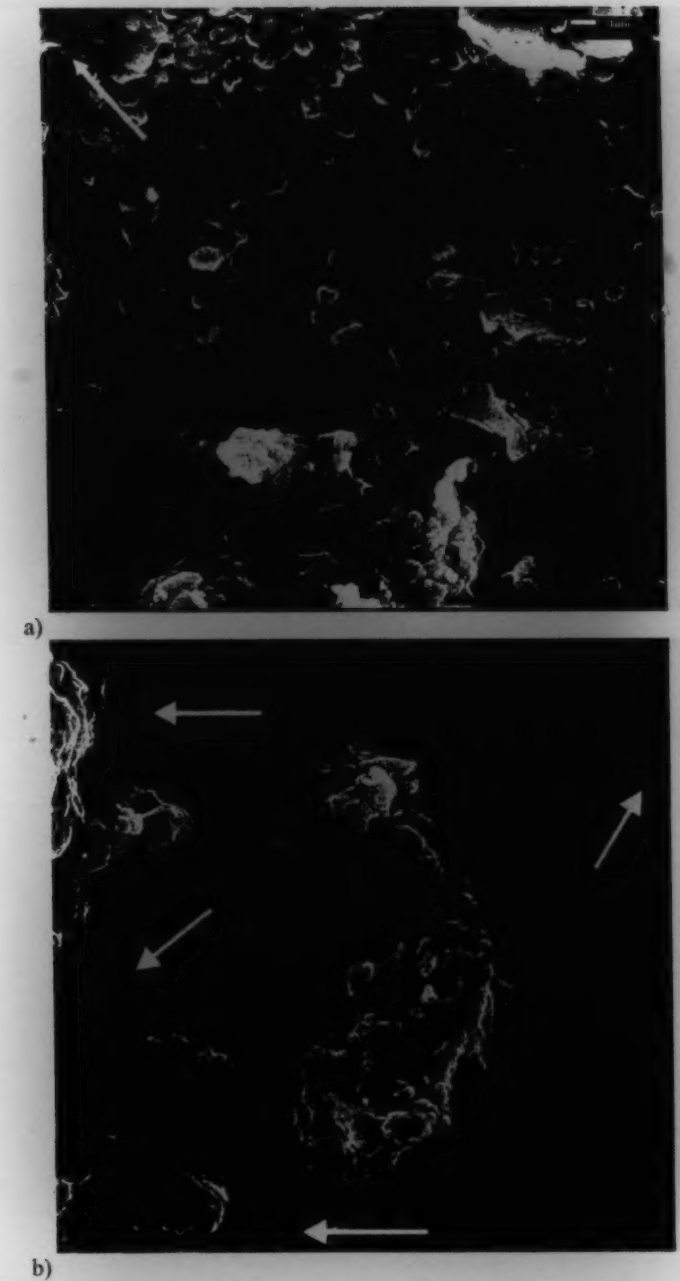


Figure 4-9 Desiccation cracks in microbial film indicate the loss of volatiles during exposure to vacuum and or electromagnetic emissions during coating and/or SEM imaging. (a) Coocoid bacteria from shallow (0.5 mbs) soil at well A4. (b) Type II calcite, bacteria and microbial film from shallow (0.5 mbs) soil near well A3.

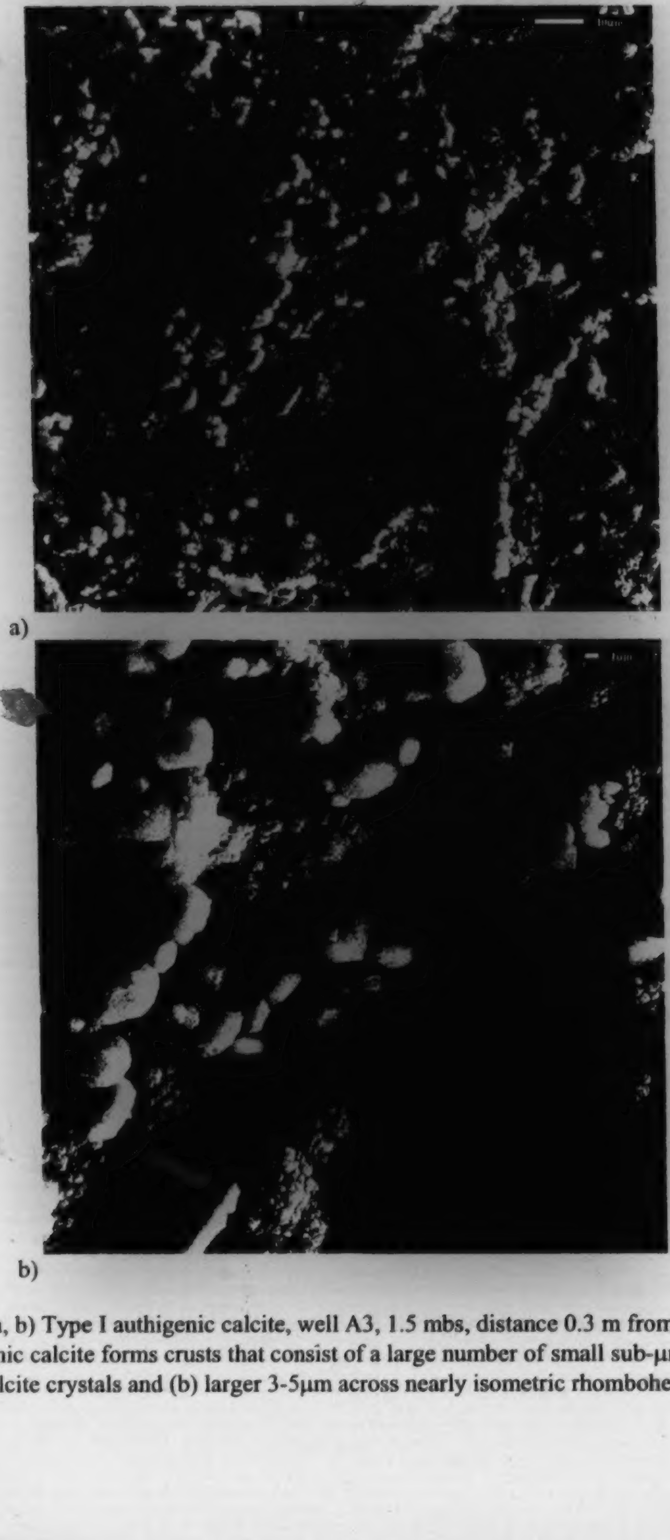


Figure 4-10 (a, b) Type I authigenic calcite, well A3, 1.5 mbs, distance 0.3 m from well bore. (a) Type I authigenic calcite forms crusts that consist of a large number of small sub-µm sized equigranilar calcite crystals and (b) larger 3-5µm across nearly isometric rhombohedra.

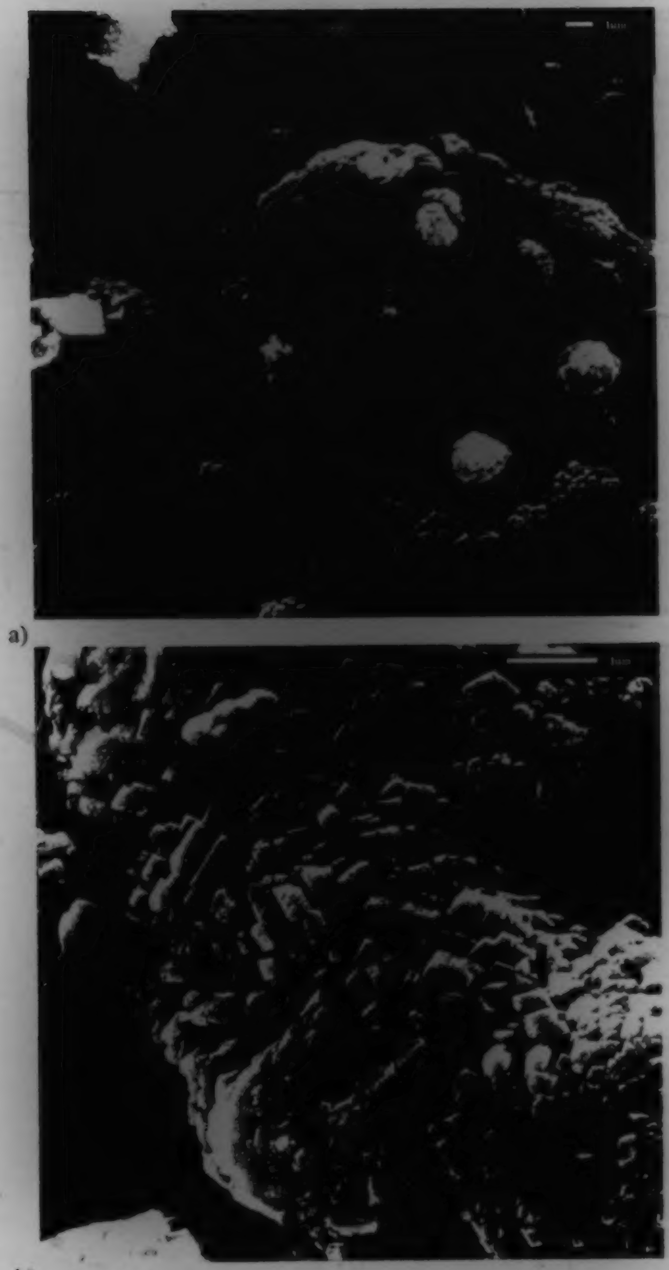


Figure 4-11 (a, b) Type I authigenic calcite from well C4-15 at Aberfeldy. The size of the individual grains and the sparry morphology of the authigenic calcite that precipitates on the well bores is similar to those of type I authigenic calcite in the soils near well A3 at Edam. The only difference is that at Aberfeldy there are no large rhombohedral grains.

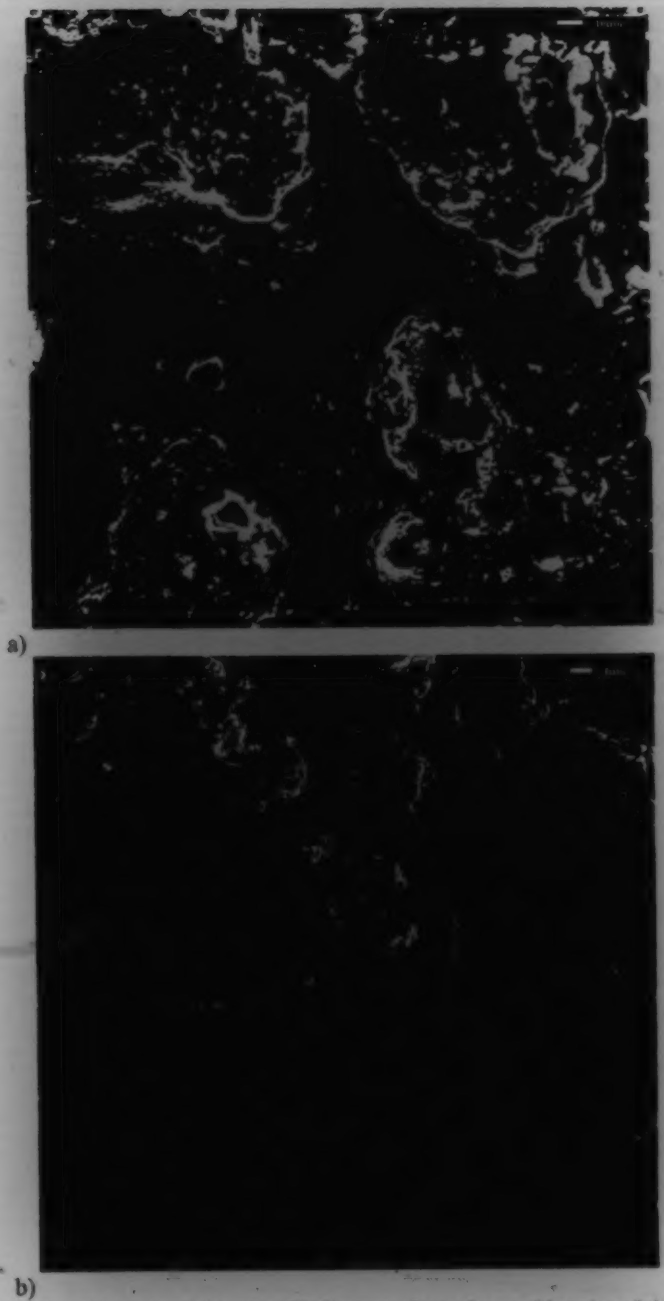


Figure 4-12 Type II authigenic calcite. (a) "Flat" crust of massive authigenic calcite coats the surface of a mineral grain. (b) Highly porous calcite aggregate grows along the surface of another grain. Microbial film covers large parts of (a) and could also bee seen on parts of (b). Samples from 0.5 mbs and 0.3 m away from well A3.

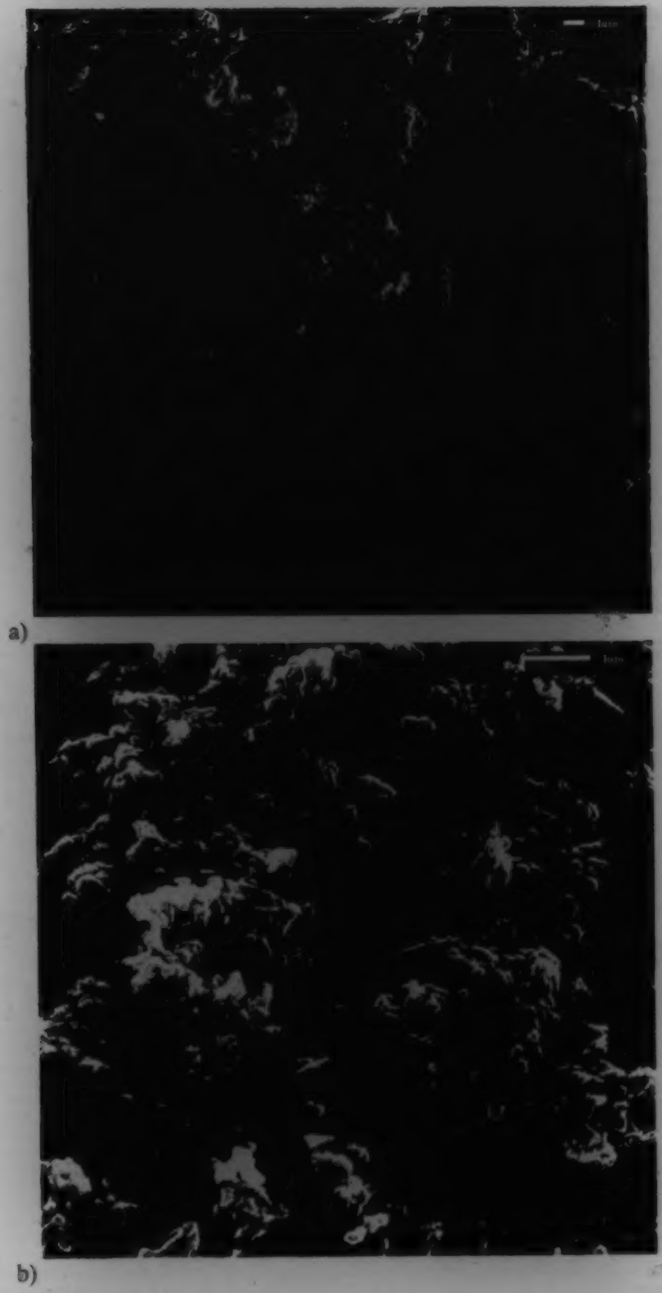


Figure 4-13 Porous type II calcite aggregates. (a) Well A3, Edam. (b) A sample of a carbonate pendant from the shallow gravel cover at well A10, Maidstone exhibits similar morphologies but grains also show evidence of mild etching and dissolution (rounded edges of the mineral grains).

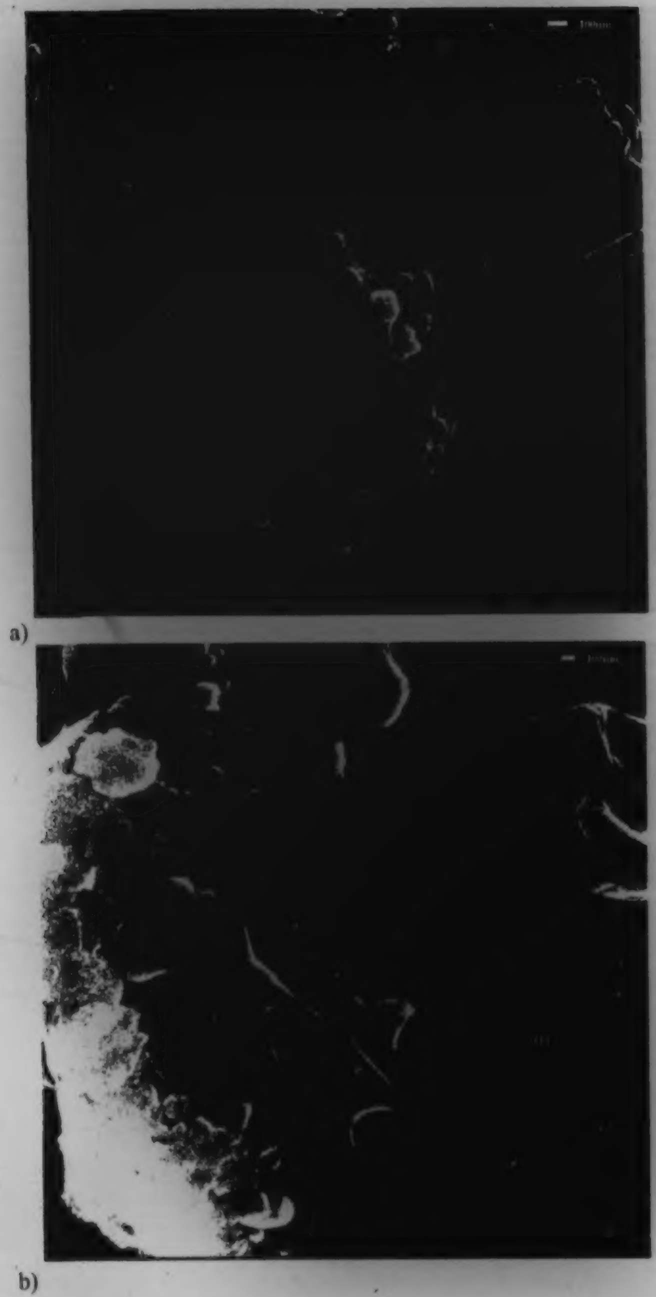


Figure 4-14 (a, b) Irregular, rounded, cauliflower-like nanometre scale textures are typical for the initial stages of type II calcite growth. Note the bacteria and abundant microbial film associated with calcite.

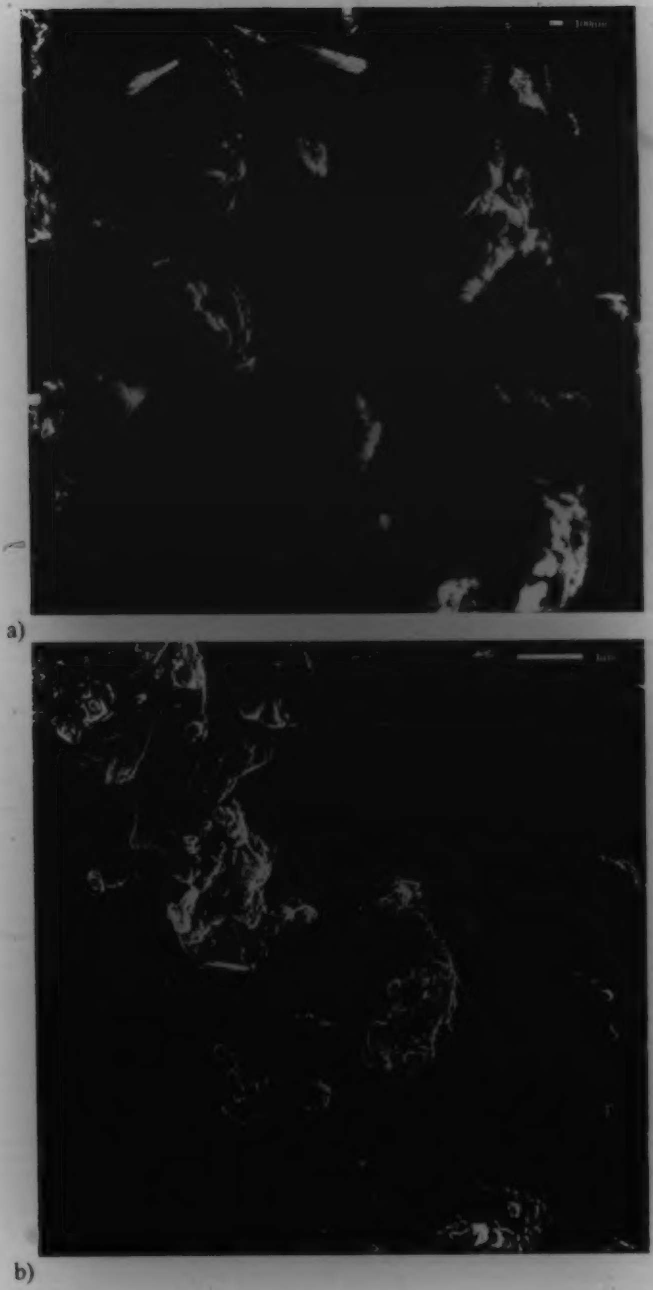


Figure 4-15 (a) Calcite growth starts as nanoscale rounded, cauliflower particles that coalesce to form porous structures composed of (b) more crystalline aggregates. Well A3, 0.5 mbs, 0.3 m away from well bore.

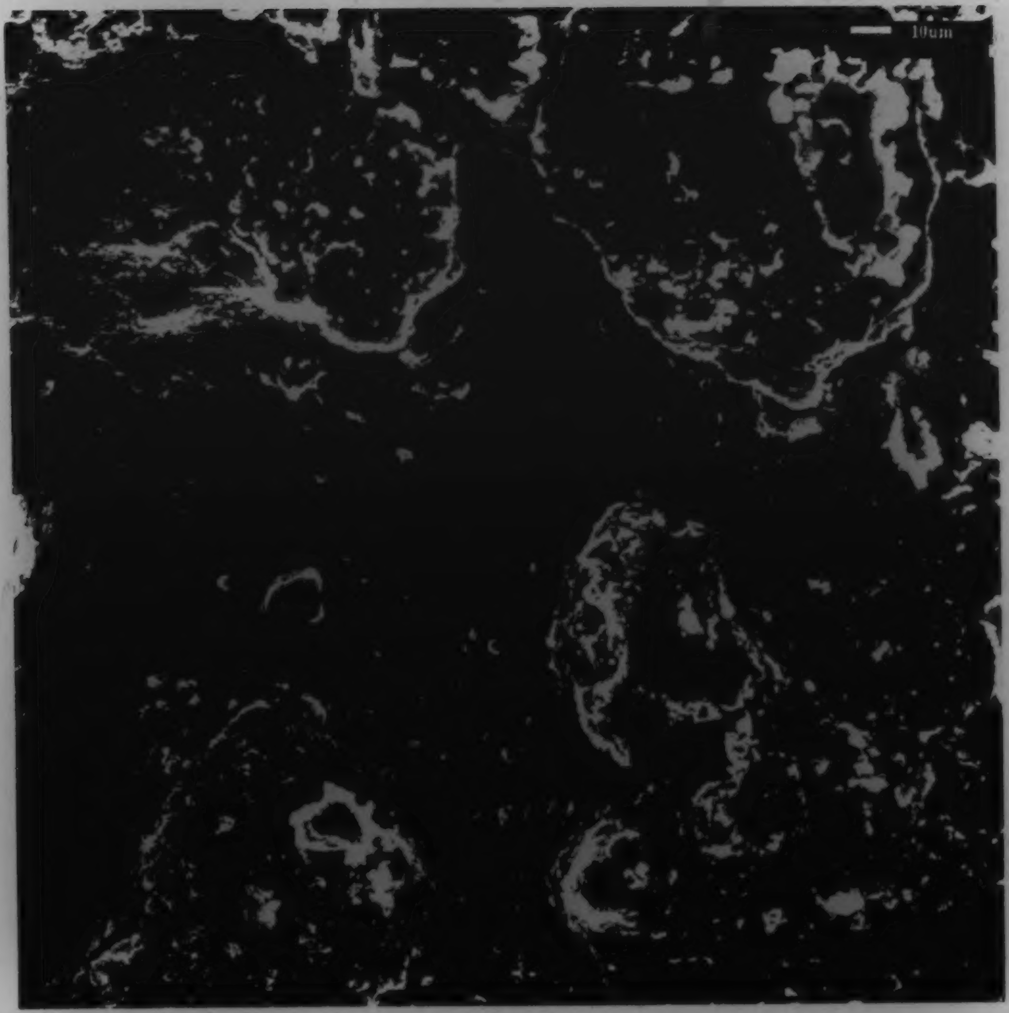


Figure 4-16 Area of "flat" type II calcite growth in a sample collected at 0.5 mbs, well A3.

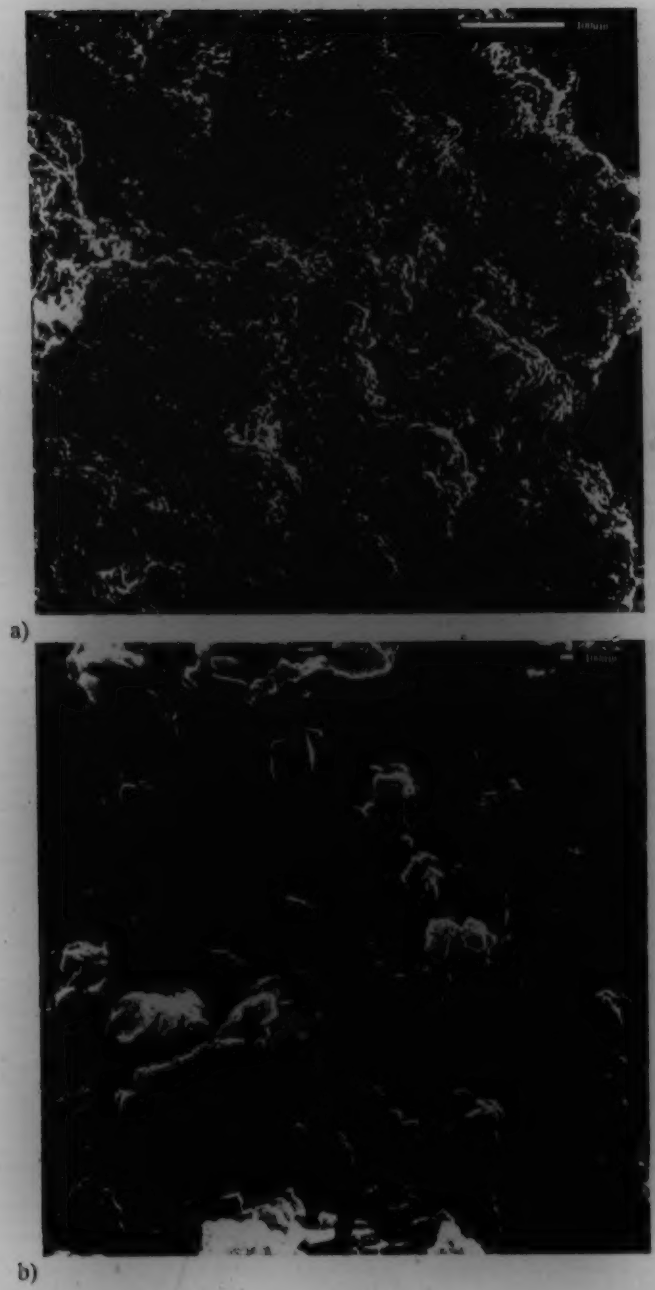


Figure 4-17 Type II calcite pendant at low (a) and higher (b) magnification. Well A10 – surface. The highly porous morphology is similar to this of porous type II calcite from the active zones of hydrocarbon oxidation near well A3. (b) A close up shows similar rounded textures with some evidence of dissolution.

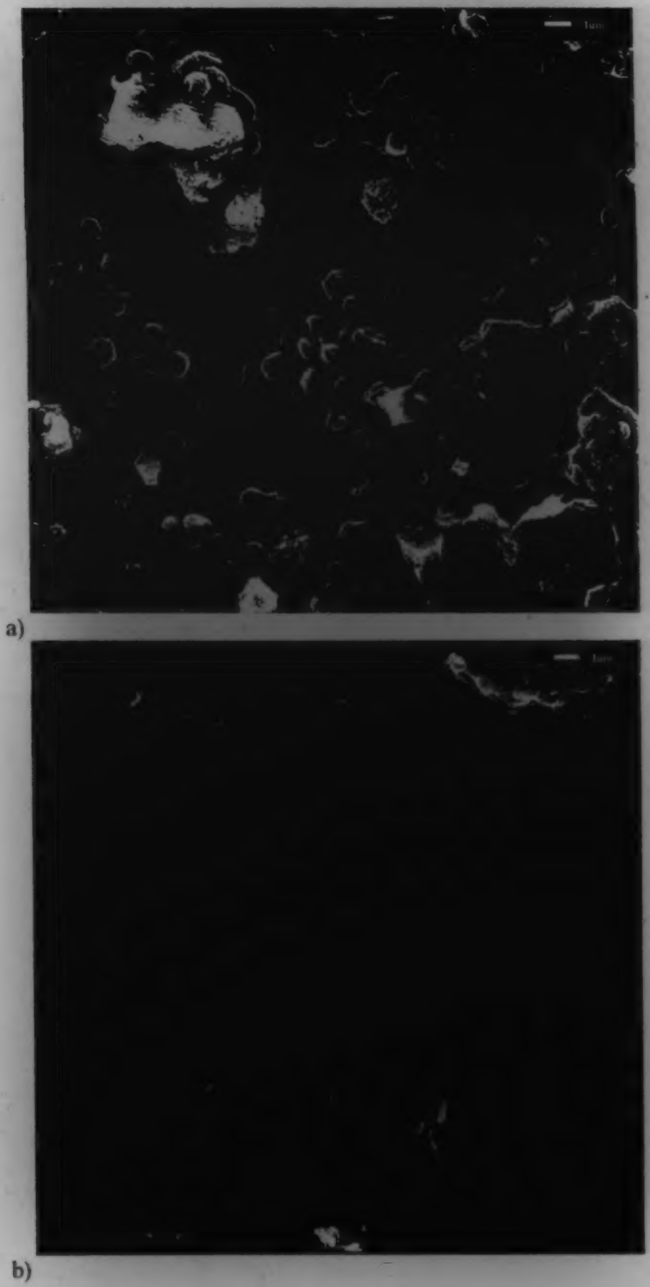


Figure 4-18 Carpets of cocci with rare rods in abundant microbial film (a) samples from A3 and (b) A4 wells. Most cocci in both samples also show evidence of desiccation. (b) Some several micrometre long filament-like objects are also seen in the central part of the image from sample A4.

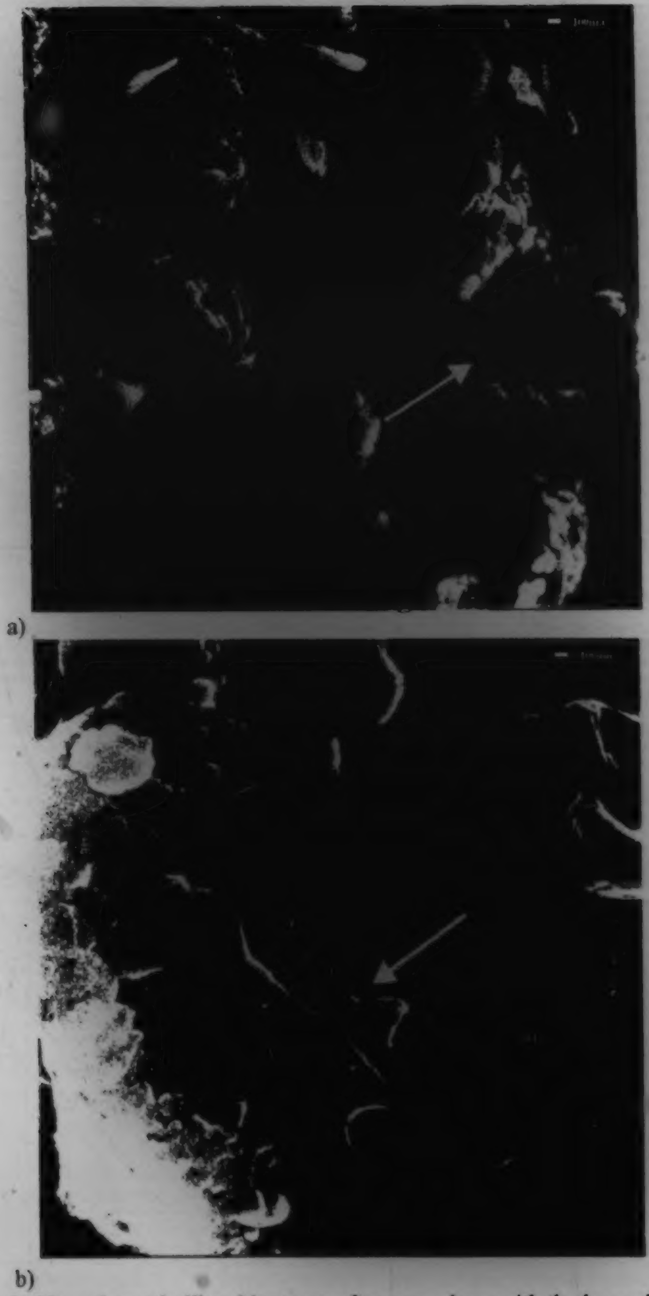


Figure 4-19 (a, b) Nannobacteria-like objects are often seen along with the larger bacteria. Their sizes are between 200 and 350 nm. The two examples shown here suggest cellular division (a, b) and the one individual shown on (b) demonstrates desiccation, that indicates that the small spheres could be unicellular organisms.

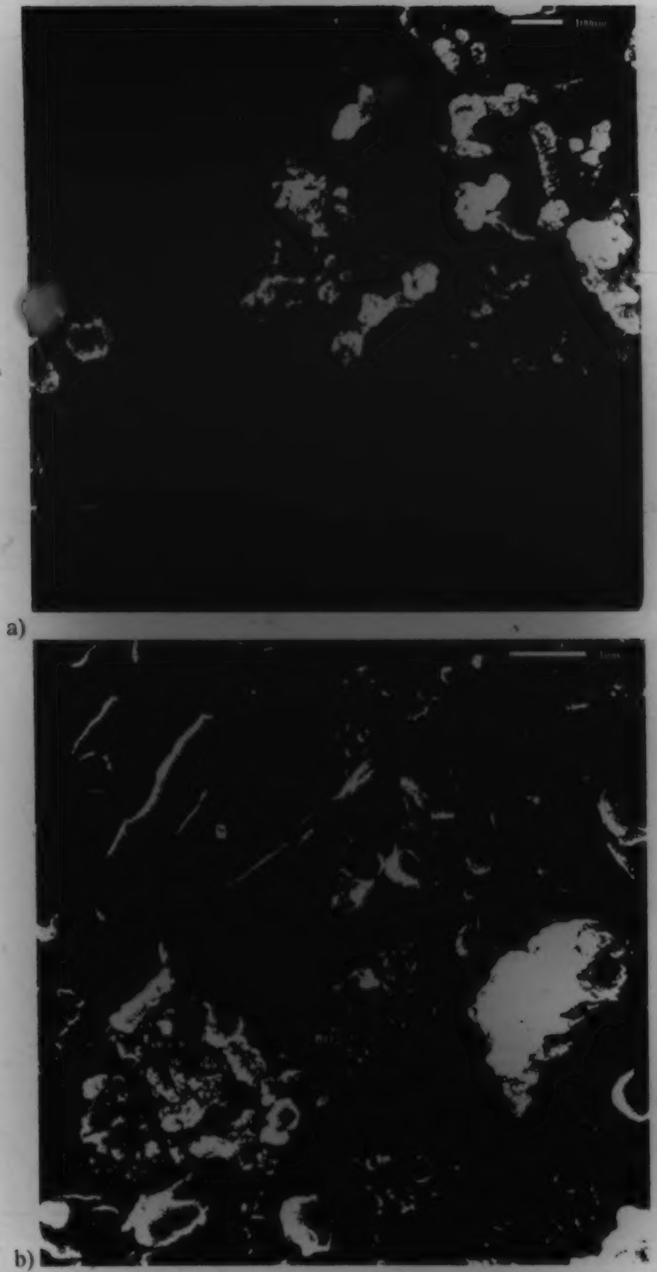


Figure 4-20 (a) A colony like aggregate of nano-scale rod structures of unknown origin. (b) Large rods (1.8-2.2 µm), apparently deceased on the surface of type II authigenic calcite with abundant microbial film. Both pictures are from well A3 samples collected at collected 0.3 m away from the well but at different depths. (a) is at 1.0 mbs whereas (b) is collected at 0.5 mbs.

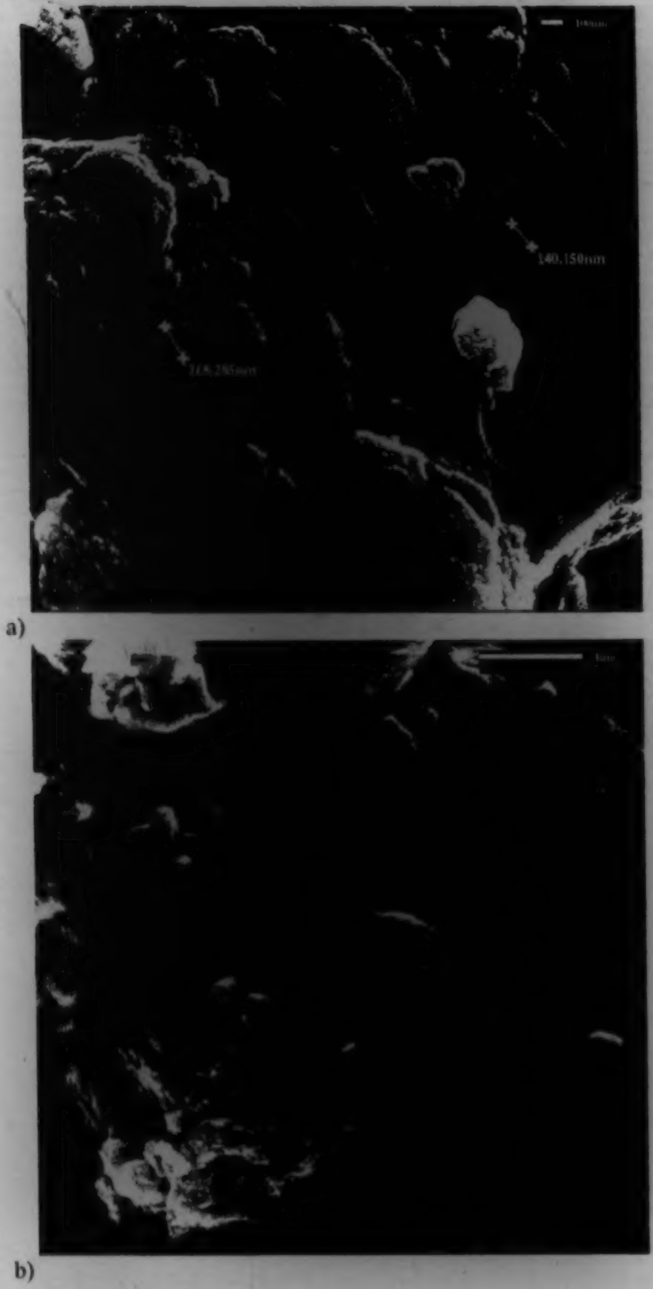
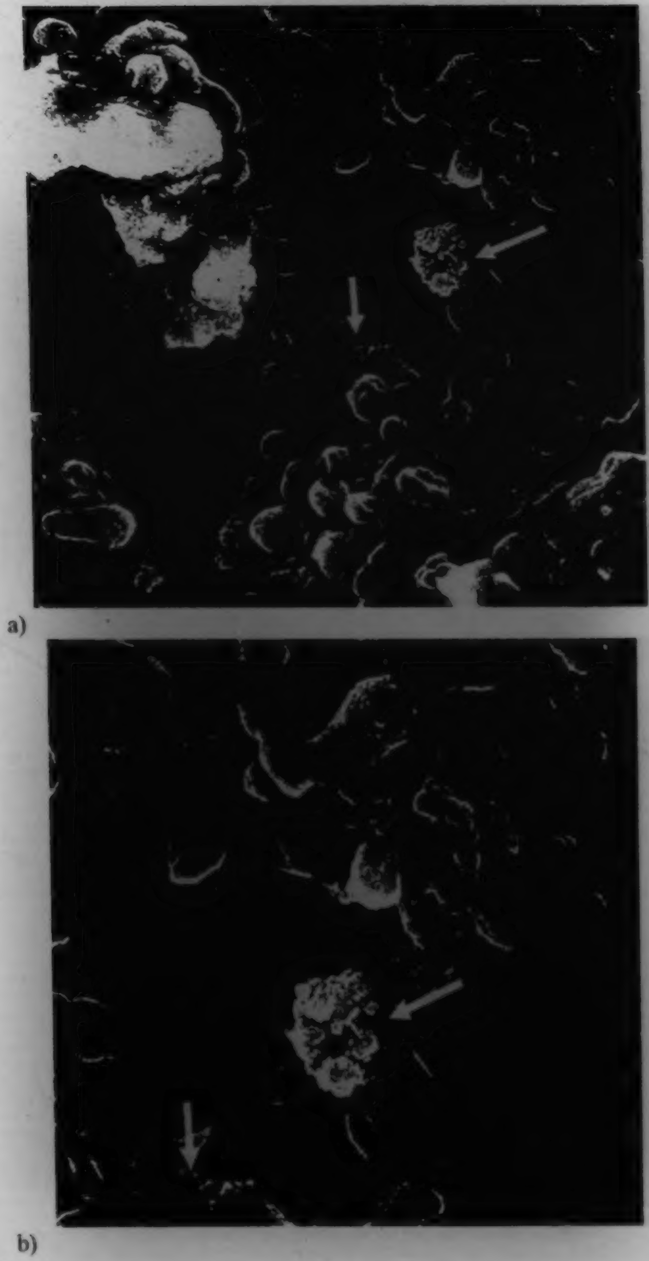


Figure 4-21 (a) Filamentous structures of possible biological origin are rarely found. (b) Microbial film covers this mixed clay calcite aggregate at 2.0 mbs immediately to the well bore at A3 well. No bacteria were found in this sample.



a)

b)

Figure 4-22 (a, b) Evidence of incipient calcite growth on top of bacteria (magenta arrows) and also on top of the bacteria/microbial film carpet in the sample (yellow arrows). Well A3, 0.5 mbs 0.3 m away from well bore.

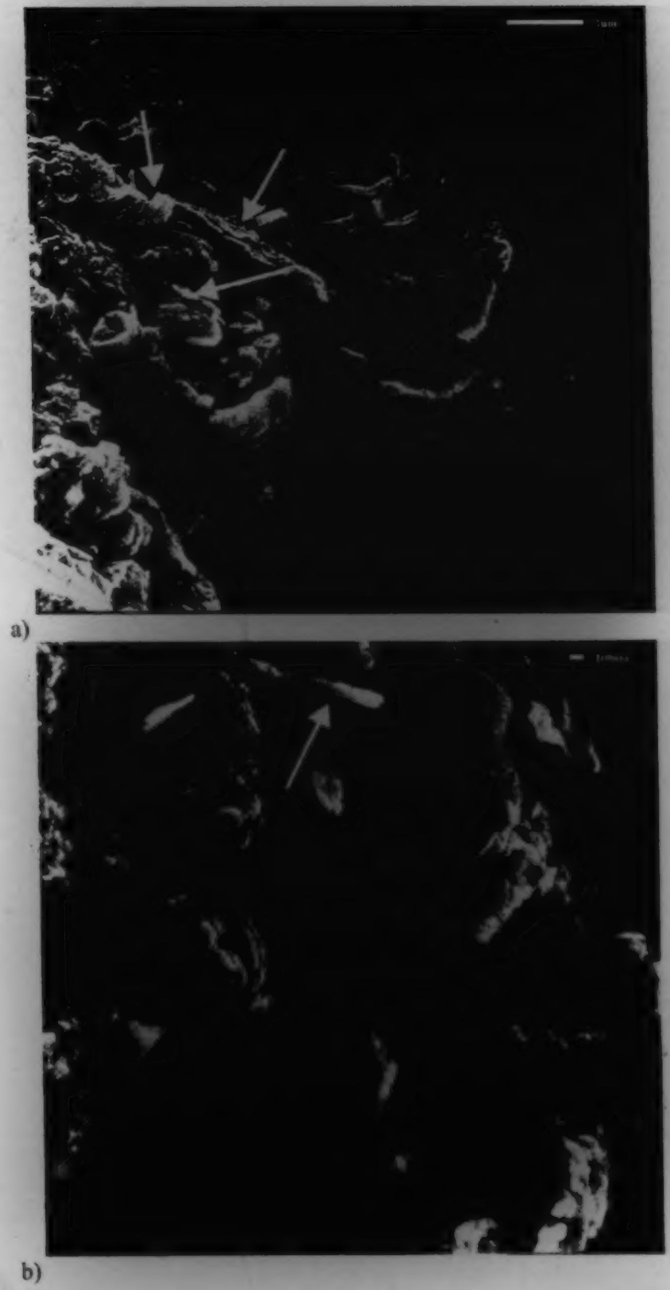


Figure 4-23 (a, b) Calcite crusts, apparently growing on top of bacteria and microbial film broken and dismembered likely due to natural processes of growing and/or the desiccation of bacteria when exposed to the high vacuum during coating or SEM imaging. Sample from the soil near well A3, 0.5 mbs, 0.3 m away from well bore.

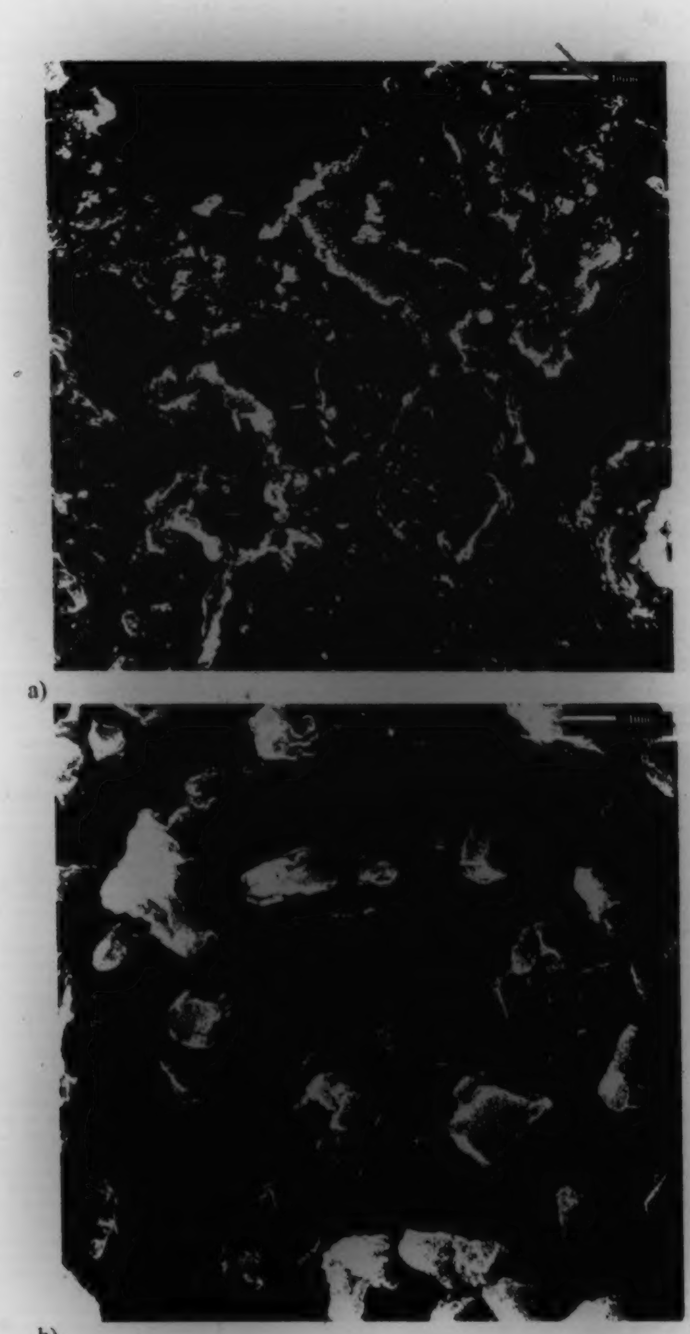


Figure 4-24 (a) Flat crusts have domains of highly porous calcite. (b) A close up of one such porous domain shows columnar structures identical to these of the aggregates that bridge mineral grains. Well A3, 0.5 mbs, 0.3 m distance from the well bore.

Chapter 5

Factors that control the stable isotope composition of soil carbonates and soil organic matter in soil not contaminated with hydrocarbons near the leaking well sites

Introduction

Carbonate minerals in soils could be of detrital and authigenic origin. Detrital carbonates comprise fragments of carbonate minerals or rocks (e.g., dolomite, limestone, etc.) that are a part of the mineral framework of the soil. Authigenic carbonates precipitate as a result of inorganic (or biological) processes in soils in semi-arid to arid areas dominated by grassy to low shrub vegetation, where the amount of annual precipitation is less than 750 mm (Cerling, 1984). The $\delta^{13}C$ and $\delta^{18}O$ of soil carbonates in bulk soil samples depend on a variety of parameters, with mechanical mixing of detrital and authigenic carbonates being one of the most important. The $\delta^{13}C$ and $\delta^{18}O$ compositions of bulk soil samples are used to estimate the fraction of authigenic carbonate (Salomons and Mook, 1976). Detrital carbonate compositions are estimated by either analyzing the stable isotope composition of soil lithic clasts or by assuming that detrital carbonates are of marine origin and thus have $\delta^{13}C$ and $\delta^{18}O$ of ca. 0 ‰ (VPDB). However, the oxygen and sometimes carbon stable isotope compositions of marine carbonate minerals are invariably modified (sometimes significantly) during diagenesis and subsequent sedimentary basin evolution and/or metamorphism (O'Neil, 1987). Therefore, the $\delta^{18}O$ and $\delta^{13}C$ of detrital carbonate in soil should be constrained before the fraction of authigenic carbonate is estimated.

Despite widespread evidence of the involvement of plants and microorganisms, carbonate precipitation is still considered a predominantly inorganic process (Monger *et al.*, 1991; Cailleau *et al.*, 2005; Lal and Kimble 2000). Estimated rates of authigenic carbonate precipitation in soil are slow (e.g., 10^{-6} to 10^{-5} moles/cm^2/year) and it is, therefore, assumed that authigenic carbonates precipitate in isotopic equilibrium with soil CO_2 and soil moisture (Cerling, 1984). Major factors that control the concentration and carbon isotopic composition of soil CO_2 include $\delta^{13}C$ of soil organic matter (SOM), soil respiration rates and physical properties of the soil (free air porosity, moisture, and temperature). The $\delta^{13}C$ of SOM depends on the proportion of C_3, C_4 and/or CAM plants that have contributed organic matter to the soil column (Cerling, 1984). Another important parameter that controls the concentration and $\delta^{13}C$ of soil CO_2 is soil respiration rate. Soil respiration is a combination of live plant root respiration and oxidation of soil organic matter by heterotrophic bacteria (Andrews *et al.*, 2000). In addition to the type and quantity of living plants and soil organic matter, soil respiration rates depend strongly on soil temperature and moisture (Boone *et al.*, 1998). The pseudo-Arrhenius relation between soil respiration rate and soil temperature renders the latter an important variable in models that aim to predict the impact of global warming on the CO_2 emissions from soil (Boone *et al.*, 1998).

By assuming that diffusion is the dominant mechanisms for mass transfer of CO_2 in soil, Cerling (1984, 1991) developed a one-dimensional mathematical model that uses the $\delta^{13}C$ of authigenic carbonates in paleosols to constrain a variety of environmental and ecological parameters. A number of studies use the diffusion model to constrain paleoclimate conditions (e.g., Cerling and Hay, 1988; Wang *et al.*, 1993; Liu *et al.*, 1996). The model is also used to estimate the amount of CO_2 in the paleoatmosphere (Cerling, 1991; Ekart *et al.*, 1999) and the quantity of trapped/lost carbon in the form of soil carbonate (Nordt *et al.*, 1998).

If parameters such as the $\delta^{13}C$ of soil CO_2 and/or SOM are known, the diffusion model can be applied "in reverse" to predict the $\delta^{13}C$ of soil calcite and to estimate soil respiration rates. The long term monitoring of the $\delta^{13}C$ of soil CO_2, soil temperature and/or soil moisture, along with $\delta^{13}C_{SOM}$ data acquired at the background site at Edam, provide an opportunity to use the diffusion model to predict the $\delta^{13}C$ of pure authigenic carbonates that would precipitate in soil in the area. Predicted $\delta^{13}C$ values are used to estimate the fraction of authigenic carbonate in background soils and to constrain the amounts and the rates of authigenic carbonate precipitation in hydrocarbon-contaminated soil at the monitoring sites (Chapters 4 and 6).

The use of the $\delta^{18}O$ of authigenic carbonate for paleoclimate reconstructions is based on the assumption of equilibrium precipitation (Stern *et al.*, 1997; Alam *et al.*, 1997; Wang and Follmer, 1998; Rowe and Maher, 2000). Thus, the $\delta^{18}O$ of authigenic carbonate should reflect the $\delta^{18}O$ of local precipitation, the seasonally dependent infiltration of the precipitation, and the impacts of evaporation and/or water rock interaction (Wang *et al.*, 1993; Tabor *et al.*, 2002). The influence that the last two variables have on the $\delta^{18}O$ of soil water depends on physical properties such as soil air permeability, grain size and lithology (Tabor *et al.*, 2002, and the references therein). Cases of extreme ^{18}O and/or ^{13}C enrichment of authigenic carbonates that form close to or at the soil surface are attributed to evaporation and/or uptake of ^{12}C from photosynthesizing organisms (Knauth *et al.*, 2003).

Paleo-temperatures determined from the isotopic compositions of authigenic carbonates are considered to reflect mean annual values (Tabor *et al.*, 2002). Although this may be a fair assessment for areas where little seasonal variability existed in the past, it is not a valid assumption for areas where seasonal variability was (is) significant. In addition, several studies demonstrate that carbonate precipitation in some paleosols occurred at a particular time of the year (Liu *et al.*, 1996; Stern *et al.*, 1997). Thus, the lack of knowledge on the timing of soil carbonate precipitation in paleosols formed under variable climate conditions could introduce significant errors in past climate reconstructions.

There are three principal goals of this chapter are: 1) to determine the amount and stable isotopic composition of detrital and authigenic carbonate in clean (background) soil away from the leaking wells; 2) to provide a better understanding of the factors that control the concentration and $\delta^{13}C$ stable isotope composition of soil respired CO_2 (and thus soil carbonates) at the background sites; 3) to determine the timing of background authigenic carbonate precipitation. The carbon and/or oxygen stable isotope composition of soil carbonates, soil CO_2, soil organic matter and soil moisture are used along with soil temperature, moisture and density data, and the diffusion model of Cerling (1984, 1991) to achieve these goals.

Results

Amounts and carbon and oxygen stable isotope compositions of background carbonates

The carbon and oxygen stable isotope compositions of 16 bulk soil samples from the saturated and unsaturated zone in areas near the leaking wells were analyzed. Five of these samples (i.e., three at Edam and two at Maidstone) were collected from the unsaturated zone (Table 5-1). The amounts of total soil carbonate, including authigenic carbonate and detrital carbonate in bulk soil samples collected away from the leaking wells, vary from 15 mg/kg to 46000 mg/kg (Table 5-1). One of the most important parameters that control the amount of carbonate is soil lithology. Sandy soil at the background location at Edam has very low soil carbonate content (e.g., from 15 to 114 mg/kg). In contrast, loamy and clayey soils at Edam and Maidstone contain between 10000 and 46000 mg/kg carbonate. The latter amounts are similar to those estimated from the Dark Brown and Black Chernozemic soils of Saskatchewan (Landi *et al.*, 2003).

The $\delta^{18}O$ compositions of background soil carbonates from the unsaturated zone vary from -0.3 to -13.9 ‰ (VPDB), whereas the $\delta^{18}O$ of carbonates from the saturated zone vary from -5.3 to -13.8 ‰, (VPDB; Table 5-1). Background soil carbonate samples collected above the capillary fringe display larger variability, and have $\delta^{13}C$ and $\delta^{18}O$ compositions lower than those of carbonates from the saturated zone (Figures 5-1, 5-2).

Concentration and $\delta^{13}C$ composition of soil CO_2

The concentration and stable isotopic composition of background soil CO_2 are presented in Table 2 and on Figure 5-3. Soil CO_2 concentrations vary throughout the sampling period and exhibit a distinct seasonal pattern (Fig. 5-3a). At 1.7 mbs soil CO_2 concentrations range from 860 to 12400 ppm (average: 6300 ppm; n=13), whereas at 1.0 mbs concentrations vary from 580 to 7800 ppm (average: 2800 ppm; n=25). The $\delta^{13}C$ of soil CO_2 varies from -18.1 to -28.1 ‰ (VPDB; average: -22.5 ‰; n=15) and 1.7 mbs, and from -9.0 to -25.0 ‰ at 1.0 mbs (average: -18.4 ‰; n=26).

Carbon stable isotopic composition of soil organic matter (SOM)

The $\delta^{13}C$ composition of soil organic matter determined in three samples from the background site at Edam varies from -29.1 to -31.4 ‰ (VPDB). A variation of the $\delta^{13}C$ compositions of bulk SOM with depth is observed, with higher $\delta^{13}C$ values in the upper parts of the profiles and lower values in the lower parts. The $\delta^{13}C_{SOM}$ from soil samples collected at the same depths, but from a soil profile located 5.5 m to the east from well A3, follows a similar pattern (Fig. 5-4).

Oxygen isotopic composition of local precipitation, soil moisture and groundwater

The $\delta^{18}O$ of the monthly and the weighted mean annual precipitation for west-central Saskatchewan used in this study are estimated using the on-line calculator by Bowen and Revenaugh (2003). The extreme seasonal temperature variation in west-central Saskatchewan brings about a significant annual variation in the $\delta^{18}O$ compositions of local precipitation. The $\delta^{18}O$ of the precipitation at Edam and Maidstone varies from -13.0 ‰ in July to -28.6 ‰ in January, with a weighted annual average value of -16.3 ‰ (VSMOW; Table 3-5).

Loss of water through evaporation results in significant enrichment of the residual soil water with ^{18}O, which may result in large differences between the $\delta^{18}O$ of local precipitation and local soil moisture (Quade and Cerling, 1995). The $\delta^{18}O$ composition of soil water was determined by using both direct and indirect methods. The direct method involves the determination of $\delta^{18}O$ of soil moisture by equilibration with CO_2 (McConnville *et al.*, 1999), whereas the indirect method involves measurements of the oxygen stable isotopic composition of soil CO_2 (Allison *et al.*, 1987). Due to rapid equilibration (seconds to minutes), the $\delta^{18}O$ of soil CO_2 is in isotopic equilibrium with soil moisture (Allison *et al.*, 1987; Amundson *et al.*, 1998). Therefore, after a temperature correction, the $\delta^{18}O$ of soil CO_2 can be used as a reliable proxy to the $\delta^{18}O$ of soil moisture (Amundson *et al.*, 1998). The $\delta^{18}O$ of soil CO_2 collected from soil gas probes installed in the microaerophilic soil near wells A3 and A4, determined on nine different occasions between January 2002 and April 2004, vary from

+22.7 to +36.0 ‰ (VSMOW). The $\delta^{18}O$ values of soil water in equilibrium with the above values were calculated using the equilibrium fractionation factor of Brenninkmeijer *et al.* (1983). At the respective soil temperatures, the $\delta^{18}O$ of soil water varies from -23.8 ‰ to -10.5 ‰ (average -15.5 ‰; VSMOW; Table 5-4). Water from the saturated zone near wells A3 and A4 was also collected in November 2003 and analyzed for $\delta^{18}O$, and the two results are virtually identical (Table 5-5). The $\delta^{18}O$ of soil water from one soil sample collected in October 2001 from the saturated zone at the background site was also analyzed, and the isotopic composition of this sample is only slightly lower than the two values reported above (e.g., -17.0 ‰; Table 5-5).

The $\delta^{18}O$ of soil moisture exhibits a distinct seasonal pattern that mimics the distribution of the estimated $\delta^{18}O$ values of local precipitation. The absolute $\delta^{18}O$ values of soil moisture, however, are higher to those estimated for local precipitation. The highest $\delta^{18}O$ composition at 1.85 mbs near well A3 is recorded in February, 2004 (e.g., -12.9 ‰) and the lowest in December, 2003 (e.g., -17.9 ‰). Average $\delta^{18}O$ of soil water at this depth is -15.3 ‰ (n=12), or one permil higher than the estimated average value of -16.3 ‰ for the weighted mean annual precipitation in the area. At 1.0 mbs near the same well, the $\delta^{18}O$ of soil moisture varies from -10.5 to -16.4 ‰ with an average value of -13.5 ‰ (n=13). For the most part, soil freezing precluded the collection of soil samples at 0.2-0.5 mbs in winter. The four data points available vary from -12.6 ‰ in November 2001 to -22.6 ‰ in April 2004. Even larger $\delta^{18}O$ variation is observed in the soil profile near well A4. At 1.0 mbs the $\delta^{18}O$ of soil moisture varies from -13.7 ‰ in August 2003 to -20.7 ‰ in April 2004. It appears that soil moisture at the two wells has similar isotopic compositions in the summer, but the $\delta^{18}O$ at well A4 is about 3 permil lower in winter. A shallow (e.g., 0.2 mbs) sample collected in August 2003 has $\delta^{18}O$ of -12.9 ‰, whereas another shallow sample from February 2004 is nearly 11 ‰ lower (i.e., -23.8 ‰).

Discussion

Stable isotopic compositions and the origin of carbonates from the saturated zone

Soil carbonate samples collected below the water table at Edam and Maidstone have distinct isotopic compositions which, for the most part, differ from those of background carbonates from the unsaturated zone or from carbonates in the microaerophilic and oxygen-rich soils around the wells (Chapter 6). Carbonates from the saturated zone are expected to have $\delta^{13}C$ and $\delta^{18}O$ values that reflect those of the detrital carbonate component in the glacial sediments that were precursors to modern soils in Western Canada. The glacial sediments in Saskatchewan comprise mixtures of Paleozoic dolomite, Cretaceous shales of predominantly marine origin and Proterozoic metamorphosed granitoids (Landi *et al.*, 2003). Therefore, detrital carbonates from the saturated zone at Edam and Maidstone should be of predominantly marine origin.

The $\delta^{13}C$ and $\delta^{18}O$ of background carbonates from the saturated zone fall within the range of $\delta^{18}O$ and $\delta^{13}C$ values of soil carbonates collected in Western Canada (Fig. 5-1; 5-5; Landi, 2002). The field includes approximately 180 bulk soil and extracted authigenic and/or detrital calcite and dolomite samples collected from various locations in Saskatchewan and Alberta (Cerling and Quade, 1993; Kohut *et al.*, 1995; Wang and Anderson, 1998; Landi, 2002). The largest data set is that of Landi (2002), with samples collected from several different types of non-agricultural soils throughout south and central Saskatchewan. Most are bulk soil samples and thus likely comprise mixtures of authigenic and detrital carbonate (Landi, 2002). The data set of Landi (2002) also includes pendants - caliche-like layered calcite that forms on the bottom of lithic clasts of gravel to pebble to cobble sizes (Wang and Anderson, 1998). Pendants have the lowest $\delta^{13}C$ and $\delta^{18}O$ and appear to be the purest form of authigenic carbonate in the soil profiles (Fig. 5-5).

The comparatively low $\delta^{13}C$ and $\delta^{18}O$ values of samples collected from the saturated zones at Edam and Maidstone suggest that saturated sediments at Edam contain post-diagenetically modified marine carbonate. An alternative explanation is that the samples contain paleo-authigenic carbonates.

Marine carbonates in sedimentary basins undergo post-diagenetic isotope exchange that could significantly alter their primary compositions (O'Neil, 1987). Most vulnerable to isotope exchange are fine-grained carbonates in sediments of predominantly siliciclastic lithologies (e.g., shales, sandstones and conglomerates). Marine carbonates from siliciclastic formations in the Western Canadian Sedimentary Basin (WCSB) often have $\delta^{18}O$ values lower than 0 ‰ (sometimes as low as -12 ‰; Longstaffe, 1987), apparently as the result of isotope exchange.

The two principal mechanisms that can modify the isotope compositions of carbonates are diffusion and dissolution-reprecipitation reactions. Experimental studies demonstrate that carbon diffusion in calcite is unlikely at temperatures lower than 500°C, even at a geological timescale (Kronnenberg *et al.*, 1984). In contrast, oxygen diffusion under water-saturated conditions is orders of magnitude faster and may occur at much lower temperatures, especially in the presence of Mn and/or Fe impurities in the calcite lattice (Kronnenberg *et al.*, 1984). Dissolution and re-precipitation of carbonate minerals requires presence of a migrating aqueous phase and/or transient PVT conditions. Stable isotope compositions of newly formed carbonates, thus, depend on the stable isotope composition and the volume of reacting fluid, as well as on the ambient temperature at the time of precipitation.

The highest $\delta^{13}C$ compositions of soil carbonate samples from Western Canada (Fig. 5-5) overlap with the $\delta^{13}C$ values of detrital dolomite samples collected in Alberta soils, suggesting that the former consist of close to 100 % detrital carbonate of marine origin (Fig. 5-5; Miller *et al.*, 1987). The $\delta^{18}O$ compositions of both the high $\delta^{13}C$ soil carbonates, and the detrital carbonates, however, reveal that these underwent significant oxygen isotope exchange. However, the $\delta^{13}C$ (and $\delta^{18}O$ compositions) of the carbonate samples from the saturated zone at both Edam and Maidstone indicate that these carbonates underwent carbon isotope exchange too. If the saturate zone carbonates are not "old" authigenic soil carbonates, the former should, therefore, be of diagenetic origin. Diagenetic carbonates in siliciclastic lithologies, such as the Viking Formation (dolomite, calcite, ankerite and siderite) have variable $\delta^{13}C$ composition that could be as low as -12 ‰ (VPDB; Fig. 5-5; Longstaffe, 1987). Both the carbonate samples from the saturated zone collected in this study, and the majority of soil carbonates from Western Canada fall within the range of values of the Viking diagenetic carbonates (Fig. 5-5). The overlap suggests, therefore, that the amount of authigenic carbonate in Western Canadian soils may be significantly overestimated (e.g., Landi, 2002).

Carbonates from the unsaturated zone

Although the four background soil carbonate samples collected in the unsaturated zone at Edam and Maidstone fall in the range of $\delta^{18}O$ values of authigenic soil carbonates collected in Western Canada, the background carbonates have lower $\delta^{13}C$ compositions (Fig. 5-1). The three most important factors that control the carbon and oxygen isotope composition of soil carbonates are: the $\delta^{13}C$ of soil CO_2; the $\delta^{18}O$ of soil water; and soil temperature. As mentioned above, the carbon isotopic composition of soil CO_2 depends upon, not only on the composition of soil organic matter and soil respiration rate, but also on the physical properties of the soil (Cerling, 1984). The $\delta^{18}O$ composition of soil carbonate, on the other hand, is controlled by the $\delta^{18}O$ of soil moisture and soil temperature at the time of precipitation (Cerling, 1984). The importance and the influence that all those factors have on the stable isotopic composition of soil carbonates are discussed below.

Relationship between soil CO_2 and soil organic matter at Edam

Soil carbon dioxide is a mixture of two end-members soil respired CO_2[1], that is the product of root and heterotrophic bacteria respiration, and atmospheric CO_2 (Cerling, 1984; 1991). The proportions of these two depend on the rate of soil respiration, the physical properties of the soil, and the depth to surface. There is little or no isotopic fractionation during bacterial decomposition and root respiration. Thus, the isotopic composition of soil respired CO_2 reflects the isotopic composition of local soil organic matter (SOM). Differences in the masses of $^{13}CO_2$ and $^{12}CO_2$, however, lead to differences in the diffusion rates of the two molecules and eventually to isotope fractionation of soil CO_2. As a result, soil respired CO_2 has $\delta^{13}C$ that is about 4.4 ‰ higher when compared to the $\delta^{13}C$ of local organic matter (cf. Cerling *et al.*, 1984, 1991).

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[1] The term soil respired CO_2 is used here to denote CO_2 produced as a result of plant root respiration or soil bacterial metabolism. Consequently soil CO_2 is used to denote the soil pore gas that is a mixture of soil respired CO_2 and atmospheric CO_2.

The carbon isotopic composition of SOM depends on the proportion of C_4 and C_3 plants that have contributed biomass to the soil in the process of soil formation (Cerling and Quade, 1993). The C_3 and C_4 plants employ different metabolic pathways to fix inorganic carbon, i.e., Rubisco for the C_3 plants and phosphoenolpyruvate (PEP) carboxylase for the C_4 plants (Hayes, 2001). The metabolic pathways used by the C_4 plants render them more efficient at fixing carbon at high levels of light and water stress, and also at low CO_2 atmospheric concentrations (Cerling and Quade, 1993). As a result C_3 plants are common in areas of temperate climate, whereas C_4 plants are found in areas of tropical or subtropical climate.

Both metabolic pathways have preference for CO_2 molecules that contain the light carbon isotope ^{12}C and, as a result, fractionate the stable isotopic composition of atmospheric carbon incorporated in the plant biomass. The total kinetic isotope effect (KIE), which is the combination of the kinetic effects of the dominant and/or subordinate metabolic pathways, is larger for the C_3 plants (e.g. 10-22 ‰; average: 18 ‰) than for the C_4 plants (e.g. 2-15 ‰, average: 5 ‰; Hayes, 2001). Therefore, the biomass accumulated in soil as a result of the decay of C_3 plants has significantly lower $\delta^{13}C$ (-25 ‰ on average) than the biomass accumulated during the decay of C_4 plants (-12 ‰ on average; assuming an atmospheric CO_2 value of -7 ‰, VPDB[2]). The kinetic isotope effect may differ in individual plants from the same species due to local environmental factors, such as water stress, soil/air temperature, exposure to sunlight, and etc. (Ehleringer and Monson, 1993).

In contrast to the prairie regions to the south of the Canada/USA border, which are dominated by C_4 grasses, the prairies in west-central Saskatchewan are dominated by C_3 grasses (Cerling and Quade, 1993). The latter is consistent with the low carbon stable isotopic composition of SOM at the

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[1] Burning of fossil fuels in the last 200 years has depressed the $\delta^{13}C$ value of modern atmospheric CO_2 to about -8 ‰.

background site and near well A3 (e.g., ca. -30 ‰). It is worth noting that the carbon stable isotope composition of soil organic matter in Edam soils is about 2 ‰ lower than the lowest average $\delta^{13}C$ compositions of SOM in a variety of Saskatchewan soils (Landi *et al.*, 2003). The low $\delta^{13}C_{SOM}$ could be explained either by an endemic origin of the plants in the area around the wells or by the influence which local environmental factors, such as nutrient and water availability, have on the degree of $^{13}C/^{12}C$ discrimination during the inorganic carbon uptake of these plants (Ehleringer and Monson, 1993; Hatte *et al.*, 1998).

The trend towards lower $\delta^{13}C$ values of SOM in the deeper parts of the soil profiles at the background site at Edam (Fig. 5-4) is similar to trends observed in other Canadian prairie soils (Landi *et al.*, 2003; Henderson *et al.*, 2004). Shifts in the $\delta^{13}C$ composition of soil organic matter with depth, however, are expected to be positive, unless SOM from the deeper parts of the soil profile is of different origin. Radioactive isotope dating (e.g., ^{14}C) of SOM demonstrates that the recalcitrant and slowly decomposing organic matter in the lower parts of the soil profiles is often thousands of years older than the labile low-density organic matter from the upper several centimetres of the soil (Torn *et al.*, 1997). Therefore, the $\delta^{13}C$ of the organic matter from the deeper parts of the soil profiles at Edam likely reflects the $\delta^{13}C$ of plant species that dominated the area thousands of years ago. According to Henderson *et al.* (2004), decreasing $\delta^{13}C$ of SOM with depth is most likely associated with the retreat of C_3 coniferous forests that occupied the southern parts of the prairies and their gradual replaced by C_3 and C_4 grasses that migrated to the north when climate changed towards warmer and more arid conditions. This is also consistent with the hypothesis of Landi *et al.* (2003), who attributed lower $\delta^{13}C$ of soil carbonates and SOM at depths below 0.5 m in Saskatchewan soils to the dominance of C_3 plants before the hypsithermal 6600 years ago. Therefore, the trend toward low $\delta^{13}C$ values of SOM observed at Edam likely reflect climate and related floral changes in this part of the continent in the last 12000-5000 years.

An obvious explanation for the observed significant variation in the concentration and stable isotope composition of background soil CO_2 through the sampling period (Table 5-2; Fig. 5-3), is mixing of different proportions of atmospheric CO_2 and soil respired CO_2. It is possible, however, that some of the variation is the result of the introduction of soil respired CO_2 of different $\delta^{13}C$ composition from different parts of the soil column. The isotopic composition of soil respired CO_2 can be determined by using a Keeling plot (Fig.5-6a; Pataki *et al.*, 2003). In the absence of another source of CO_2 but soil respiration and atmospheric CO_2, and assuming a homogeneous $\delta^{13}C$ of the respired CO_2, soil gas samples must plot on a straight line with atmospheric CO_2 at one end and an intercept that defines the composition of soil respired CO_2 at the other end. When soil CO_2 samples from the monitoring site at Edam are plotted on a Keeling plot, these define an elongated field of triangular shape. A best-fit line through all sample points has an intercept of -23.7 ‰ that is, thus, the average $\delta^{13}C$ of soil respired CO_2 in the soil profile. As mentioned above, the diffusion related ^{13}C enrichment of soil CO_2 is 4.4 ‰ (cf. Cerling, 1984). If the average $\delta^{13}C$ value of SOM is -30 ‰, expected $\delta^{13}C$ of soil CO_2 at the background site should be ca. -25.6 ‰, or about 2 ‰ lower that the average $\delta^{13}C$ of soil CO_2 determined by the Keeling plot (e.g., -23.7 ‰). There are two reasons to explain the discrepancy. First, the average $\delta^{13}C$ of soil respired CO_2 is likely skewed towards a higher value due to missing soil gas samples from the deep soil gas probe that was frozen in winter. Second, the average $\delta^{13}C$ of CO_2, estimated from the average $\delta^{13}C$ of SOM, does not reflect the $\delta^{13}C$ of soil respired CO_2 because of differences in the isotopic composition of source soil organic matter in the soil profile, and especially in the uppermost several centimeters where the concentration of labile organic matter, likely responsible for most of the CO_2 produced in the soil profile, should be the highest. Therefore, generation of soil CO_2 from SOM of different isotopic composition in different parts of the soil column should be responsible for the observed $\delta^{13}C$ variation of soil CO_2. The large spread of data points close to the lower intercept of the Keeling plot also indicates the presence of more than one CO_2 source in the soil column. If soil CO_2 were a binary mixture of one isotopically uniform soil respired CO_2 end-member and atmospheric CO_2, samples collected at the same time but at different depths in the soil profile should have plotted along a straight line with a lower intercept that points towards the $\delta^{13}C$ composition of the soil-respired CO_2. However, this is not the case at Edam where deeper samples are consistently offset towards lower $\delta^{13}C$ values (Fig. 5-6), and shallow samples plot along a line with a less steep slope. Consequently, the average $\delta^{13}C$ of soil respired CO_2 at 1.7 mbs is -26.5 ‰ (n=11; Fig. 5-6b), whereas the average $\delta^{13}C$ of soil respired CO_2 collected at 1.0 mbs is -22.5 ‰ (n=21). The difference between the average $\delta^{13}C$ values of soil-respired CO_2 at 1.0 and 1.7 mbs is about 4 ‰. If the $\delta^{13}C$ of soil-respired CO_2 is corrected for diffusion related ^{13}C enrichment by adding 4.4 ‰, the average $\delta^{13}C$ of SOM at 1.0 and 1.7 m should be -27 and -31 ‰, respectively. The SOM in the background soil sample collected at 1.7 mbs at Edam has $\delta^{13}C$ of -31.1 ‰ that is statistically identical to the estimated average soil respired CO_2 at that depth. The match indicates that soil-respired CO_2 in the deepest parts of the saturated zone is generated by *in-situ* heterotrophic bacterial mineralization of organic matter of low $\delta^{13}C$. The estimated $\delta^{13}C$ of soil respired CO_2 in the upper part of the soil profile is about 2 ‰ higher that the measured $\delta^{13}C$ of SOM. The explanation is, again, that most of the soil-respired CO_2 is generated in the upper several centimetres of the soil profile (see Hendry *et al.*, 1999, and the references therein). Although no sample was collected at 0.2 mbs at the background site at the time, three shallow samples (e.g. at 0.2 mbs) that contain relatively ^{13}C enriched SOM (e.g., -26.4 to -27.3 ‰) are collected in oxygen-rich soils away from wells A4 and A3 (Chapter 6; Table 1-6). Estimated $\delta^{13}C$ of soil respired CO_2 is consistent with bacterial mineralization of SOM that has the above or higher carbon isotopic composition, and indicates that most CO_2 in the upper part of the soil profile at the background site is in fact produced in the upper 0.2 m either by heterotrophic bacterial metabolism or by root respiration.

In addition to the above, it is worth nothing that a significant range of Keeling intercepts, with some as high as -21.4 ‰ and some as low as -35.4 ‰, is observed. Typically the high values are recorded in winter, whereas the low values are common in summer. Although some extreme values may by the result of error propagation, alternative explanations are nevertheless possible. Values as high as -21.8 ‰ would require a contribution of biomass from C_4 or CAM plants, however, no soil organic matter of such high $\delta^{13}C$ compositions has been found. Thus, it is more likely that this number reflects isotope exchange of soil CO_2 with DIC in the groundwater. The unconfined aquifer in the area is underlain by clayey till of high detrital carbonate content (Chapter 2). During the winter, when soil respiration rates decrease, the $\delta^{13}C$ of soil respired CO_2 likely shifts towards higher values, due to exchange with DIC produced during the dissolution of carbonate from the glacial tills (cf. Tinguy and Shinje, 2002). The relatively high $\delta^{13}C$ of SOM collected in the capillary fringe at the background site at Edam is also consistent with this hypothesis. The lowest values (e.g., -35.4 ‰) determined from the Keeling plot may reflect the presence of CO_2 produced from aerobic bacterial oxidation of bacteriogenic methane generated in the shallow aquifer.

Soil respiration rates and the $\delta^{13}C$ of soil carbonates at Edam

A detailed description of the diffusion model for soil CO_2 is available in Cerling (1984, 1991) and Quade *et al.* (1990) and, therefore, will not be presented here. For the purposes of the model soil is regarded as an one-dimensional box with a lower impermeable boundary. The upper boundary (a Dirichlet-type) is set at atmospheric CO_2 concentration. To calculate the steady state distribution of CO_2 in the soil column, the production of CO_2 in the soil column Φ is expressed as a function of depth (z), i.e., $\Phi(z) = \exp(-z/z^*)$, where z^* is 0.2 m, and represents the uppermost soil horizon where most soil CO_2 is generated. The specific parameters used in the model are as follows: depth to the impermeable base (L) is 1.8 m; concentration of atmospheric CO_2 at 1.8 mbs (i.e., $L = z$) is zero; total pressure is one atmosphere; partial CO_2 pressure corresponds to CO_2 concentration of 350 ppmv; diffusion coefficient of CO_2 in air at STP conditions is 0.144 $cm^2.s^{-1}$; tortuosity has a value of 0.6 (commonly applied for sandy soils; cf. Freeze and Cherry, 1979); free air porosity of 0.4[3] is estimated from soil density measurements; and the $\delta^{13}C$ composition of atmospheric CO_2 is -8.0 ‰ (VPDB). The diffusion coefficient for CO_2 in soil (*Ds**) was calculated as a function of soil temperature, free air porosity, and tortuosity (cf. Kirkham and Powers, 1972). Soil temperature was varied within the values measured throughout the monitoring period (Chapter 3), while the $\delta^{13}C$ variability of SOM was also taken into consideration by assuming that SOM in the uppermost parts of the soil profile has a value of -25.0 ‰.

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[3] This parameter was varied to model the impact of soil freezing on soil air permeability.

Factors that control soil respiration rates

Although soil respiration rates were not measured, the diffusion model allowed these to be estimated by inserting arbitrary values into the model until a sufficiently good fit to the measured concentrations and $\delta^{13}C$ compositions of soil CO_2 at the two soil gas probes was achieved. Estimated soil respiration rate values reach 1.6 $mmol.m^{-2}.h^{-1}$, during the summer (Fig. 5-7). These values are within the lower range of values reported for arid and desert areas (Cerling, 1991), and are consistent with the sparse vegetation and low SOM content of soil in the study area. To match measured soil CO_2 concentrations and $\delta^{13}C$ compositions in winter, however, soil respiration rates comparable to and in some cases even higher than those estimated for the summer months had to be used. These high values were difficult to reconcile with the measured low to subzero temperatures in the soil column at that time of the year. Although microbial activities in northern soils may proceed at temperatures as low as -6.5°C (cf. Clein and Schimel, 1995), soil respiration rates decrease significantly in winter. Soil CO_2 concentrations, however, fall along with soil temperatures until November when they start rising until early May (Fig. 5-3b). The field observations at Edam mimic those of Solomon and Cerling (1987) from Utah mountain soils. According to Solomon and Cerling (1987), the presence of a thick snow cover reduces significantly the diffusion of carbon dioxide out of the soil in winter. The lack of (significant) snow cover at Edam, however, is not consistent with this hypothesis. In addition, changes in soil CO_2 concentrations in November and May coincide with soil freezing and thawing observed at the site. Thus, soil freezing appears to be responsible for the observed variability in carbon dioxide concentrations in winter. However, observations in sandy soil at a similar field site near Saskatoon (Hendry *et al.*, 1999) show little or no effect of soil freezing on carbon dioxide concentrations. Measured volumetric soil moisture content in the upper 0.5 m of two soil profiles, both located at 4.0 m away from wells A3 and A4 at Edam, in October and November 2001 and 2003 are similar to or higher (e.g., 4 to 15 %) than those measured at the site near Saskatoon (Chapter 3; Table 3-4). Thus, it is possible that the higher soil moisture contents of the shallow soil at Edam help to form a less permeable frozen layer at the site in the winter.

Elevated soil CO_2 concentrations in winter (Fig. 5-3b) suggest that heterotrophic bacterial respiration continues in the lowermost parts of the soil profile or even, perhaps, in the groundwater. A rise of soil CO_2 concentrations accompanied by decreasing $\delta^{13}C$ of soil CO_2 in April 2003 coincides with a rapid rise of soil temperature, and indicates renewed soil respiration in the lower parts of the soil profile. A subsequent decrease of the concentrations of soil CO_2 and a concomitant rise of $\delta^{13}C$ of CO_2 in the samples collected in May 2003 coincide with the complete thawing of the soil, and it is likely caused by the release of CO_2 trapped in the lower soil horizons that is followed by an influx of and mixing with atmospheric CO_2 and/or higher $\delta^{13}C$ CO_2 from the upper soil horizon. In addition, a decrease of the $\delta^{13}C$ of soil respired CO_2 at low temperature, observed in samples collected at 1.7 mbs, indicates that soil respiration and production of CO_2 of higher $\delta^{13}C$ in the upper parts of the soil diminishes significantly in the fall, while the production of low $\delta^{13}C$ soil CO_2 in the lower soil horizons continues.

The relationship between soil temperature and respiration rate is plotted on Figure 5-8. On several occasions in the summer of 2002 and 2003, measured soil CO_2 concentrations at 1.0 mbs were significantly lower than those predicted by the diffusion model. As a result, estimated respiration rates at 1.0 mbs were lower than those estimated at 1.7 mbs. The corresponding lower soil CO_2 concentrations indicate that the upper parts of the soil profile are either having higher air permeability due to reduction of soil moisture levels, or that CO_2 production in these parts of the soil slows down, or both. Persistent dry conditions induce water stress that can significantly depress respiration rates (Lavigne *et al.*, 2004). Water stress has a larger effect on root respiration than on heterotrophic respiration (Pendal *et al.*, 2003). The site where the background soil gas probes are installed is sparsely vegetated, and evaporation in summer can be very high. Soil moisture contents measured on samples from this site collected in June 2002, vary from 7 % at 0.5 mbs to 18 % at 1.5 mbs (Chapter 3), and are consistent with water stress conditions in the upper parts of the soil column. Large variance in soil moisture also implies heterogeneous effective porosity of the soil profile. Therefore, the discrepancy between modeled and measured soil CO_2 contents in the late summer is likely to be caused by the combined effects of water stress and higher air permeability in the upper parts of the soil profile. A similar trend of calculated CO_2 fluxes is reported from sandy soils by Hendry *et al.*, (1999) at their site near Saskatoon. These are important observations because they highlight a negative feedback mechanism that counteracts the influence of increasing soil temperature on soil CO_2 production in sandy soils.

To determine the timing of soil carbonate precipitation, different soil respiration rates are used and the resulting estimated $\delta^{13}C$ values of authigenic soil carbonates are compared to the $\delta^{13}C$ values of real carbonates from the soil profiles at Edam. The modeled $\delta^{13}C$ values match measured $\delta^{13}C$ values best at or around soil respiration rates of about 0.8 $mmol.m^{-2}.h^{-1}$ (Figure 5-9). The match suggests that soil carbonates formed at or around soil respiration rate values of 0.8 $mmol/m^2/h$, and not at higher rates. Therefore, background soil carbonates at Edam appear to be 100 % authigenic carbonate formed in the summer when both evaporation and/or evapotranspiration are high, and respiration rates are low, likely due to water stress.

Lack of data on the composition of soil gas and soil organic matter and the physical properties of soils at Maidstone renders the interpretation of the stable isotopic compositions of carbonate samples collected at this site, more difficult. Two samples collected at 0.5 mbs have similar $\delta^{13}C$

compositions (e.g., -12.0 and -11.4 ‰). The $\delta^{13}C$ of these samples is lower than that of Edam samples collected at the same depth. This is likely due to the higher soil respiration rates and/or lower air permeability of Maidstone soils. Carbon isotope compositions of ca. -12 ‰ are consistent with calcite precipitation from soil CO_2 having carbon stable isotopic composition of -23 ‰, and indicate that soil organic matter at the site is largely of C_3 plant origin.

$\delta^{18}O$ of precipitation, soil water and the $\delta^{18}O$ of background soil carbonate

The $\delta^{18}O$ of soil carbonates that would precipitate at 0.2-0.5, 1.0 and 1.7/2.0 mbs at different times of the year is estimated using the $\delta^{18}O$ of soil moisture estimated near wells A3 and A4, soil temperature, and the fractionation equation of Kim and O'Neil (1997). The $\delta^{13}C$ compositions of soil samples collected at 0.5 and 1.5 mbs suggest that these consist of 100 % pure authigenic calcite. In contrast, the sample collected at 2.0 mbs is likely of detrital origin. The $\delta^{18}O$ of the soil carbonate sample (e.g., -8.5 ‰, VPDB) collected at 0.5 mbs indicates that it should have formed at temperatures close to freezing, if equilibrium with measured $\delta^{18}O$ of soil moisture at Edam is assumed. Although presence of detrital carbonate in the sample may explain the elevated $\delta^{18}O$ value, it is not consistent with the measured $\delta^{13}C$ value of calcite that coincides with that estimated by the diffusion model. Alternatively, calcite with the above oxygen isotopic composition precipitated at higher soil temperature, from soil water that originated as summer precipitation (e.g., -13 ‰, VSMOW) and was then subjected to ca. 20 % evaporation, resulting in ^{18}O enrichment of ca. 5 ‰ (Clark and Fritz, 1997). The soil carbonate sample at 1.5 mbs also has a relatively high $\delta^{18}O$. Estimates indicate that if soil carbonate at this depth consists of 100 % authigenic calcite (as suggested by its $\delta^{13}C$ composition), it must have precipitated from soil water that originated as summer precipitation and also underwent between 15 and 17 % of evaporation. Evaporative enrichment at the background site is consistent with the high air permeability estimated in the soil profiles at Edam and also with the sparse vegetation at the site. Although such high $\delta^{18}O$ compositions of soil moisture have not been measured in the past two years, high $\delta^{18}O$ compositions of carbonate pendants, especially those collected in the southernmost Brown soil zone in Saskatchewan (Landi, 2002) indicate that evaporative enrichment of soil water is a common phenomenon.

The two samples collected at 0.5 mbs at Maidstone have very different $\delta^{18}O$ compositions (e.g., -13.8 and -5.3 ‰, respectively Table 5-1, Fig. 5-1). The first sample is collected from undisturbed soil near the western edge of the A10 well lease, whereas the second is collected in the farming field nearby. The $\delta^{18}O$ composition of the first sample is in isotopic equilibrium with soil moisture of ca. -13 ‰ (VSMOW) and at soil temperatures of ca. 15°C. The high $\delta^{18}O$ of the second sample is rather unusual (Table 5-1). Similarly to the Edam samples, the low $\delta^{13}C$ of this carbonate renders possible contribution of significant amounts of detrital carbonate unlikely. Estimates indicate that in order for this carbonate to form in equilibrium with soil water at average or high soil temperatures (e.g., 10-17°C) it likely precipitated in soil water that underwent evaporation as high as 40 %. This could only be consistent with precipitation very close to the soil surface (e.g., 5-10 cm). As mentioned above, this soil sample was collected from the farming field outside the A10 well lease. Soil samples collected from farming fields, and especially those close to surface, are likely to have been disturbed by tillage, which is known to significantly increase evaporation (Quade and Cerling, 1995). Therefore, it is most likely that this authigenic calcite precipitated close to the surface and was subsequently displaced by tillage. Samples of authigenic dolomite that form as a result of extreme evaporative enrichment in shallow saline soils in east central Alberta have $\delta^{18}O$ compositions as high as -1.3 ‰ (Kohut *et al.*, 1995). The authigenic dolomites, however, have higher $\delta^{13}C$ compositions that indicate involvement of a significant percentage of atmospheric CO_2 consistent with the lack of vegetation at the site (Kohut *et al.*, 1995). In contrast, the low $\delta^{13}C$ of the sample at Maidstone indicates that CO_2 involved in carbonate precipitation must have been provided largely by decaying C_3 plant material, with little or no atmospheric input. The presence of significant quantities of C_3 biomass is not unexpected for farm fields where plant remnants, such as stems and roots, remain in the soil long after harvest. The $\delta^{18}O$ evidence of widespread involvement of evaporative enrichment in the precipitation of authigenic soil carbonates at Edam and Maidstone indicates that evaporation is the main mechanism of soil carbonate precipitation in soil away from the leaking wells.

Conclusions

The $\delta^{13}C$ and $\delta^{18}O$ of carbonates from the glacial sediments below the water table at Edam reveal that these are likely marine carbonates that underwent post-diagenetic alteration. Those carbonates are considered proxies to the detrital end-member carbonates in soils at the sites. The partial overlap of the stable isotope compositions of carbonates from the saturated zone with those of published soil carbonates in central Saskatchewan (Landi, 2002) indicates that the fraction of authigenic carbonate in many soil samples is overestimated. This casts doubt on estimates of the amounts of authigenic carbonate precipitation in Western Canada, and hence on the ability of prairie soils to scavenge and store inorganic carbon.

Soil respiration rates estimated with the diffusion model of Cerling (1984, 1991) demonstrate clear dependence on seasonality. Rates vary from nearly zero in winter to 1.6 $mmol.m^{-2}.h^{-1}$ in summer and are on the lower end for respiration rates determined for arid soils. Results also demonstrate that soil freezing plays an important role in the distribution of soil CO_2 by decreasing free air porosity by as much as one order of magnitude.

A comparison between estimated and measured $\delta^{13}C$ of the soil carbonates at Edam and Maidstone reveals that these precipitated in the summer. Summer precipitation is corroborated by the high $\delta^{18}O$ of soil carbonates indicative of the involvement of soil water evaporation in carbonate precipitation. This is consistent with a number of studies that establish authigenic soil carbonate precipitation during the warmest and driest months of the summer (e.g., Liu *et al.*, 1996, and the references therein).

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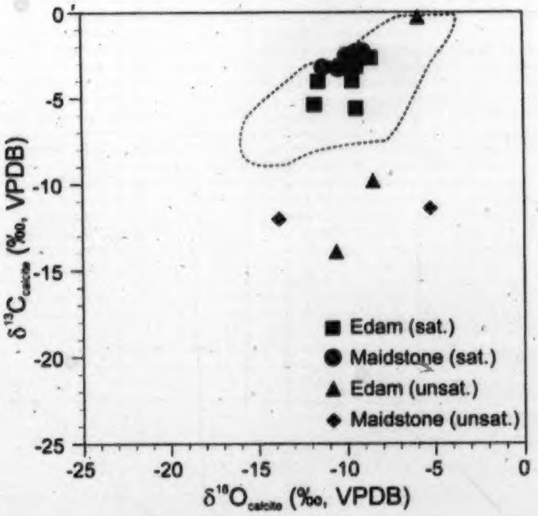

Figure 5-1 Oxygen vs. carbon stable isotope compositions (‰, VPDB) of soil carbonates at the background sites at Edam and Maidstone. The outlined field encompasses published and unpublished $\delta^{13}C$ and $\delta^{18}O$ compositions of authigenic soil carbonates from Saskatchewan and Alberta (Fig. 5-5).

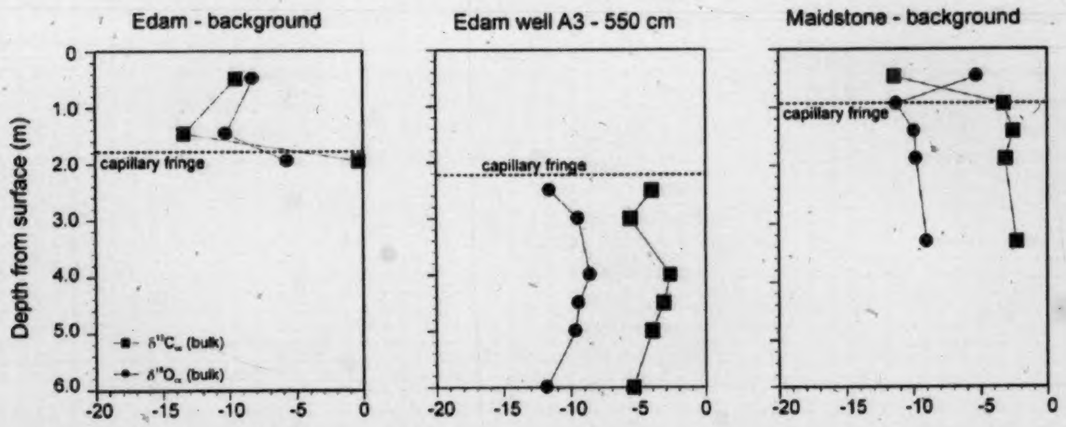

Figure 5-2 Carbon and oxygen stable isotope compositions of bulk soil carbonate samples from the saturated and unsaturated soil at the background sites at Edam and Maidstone.

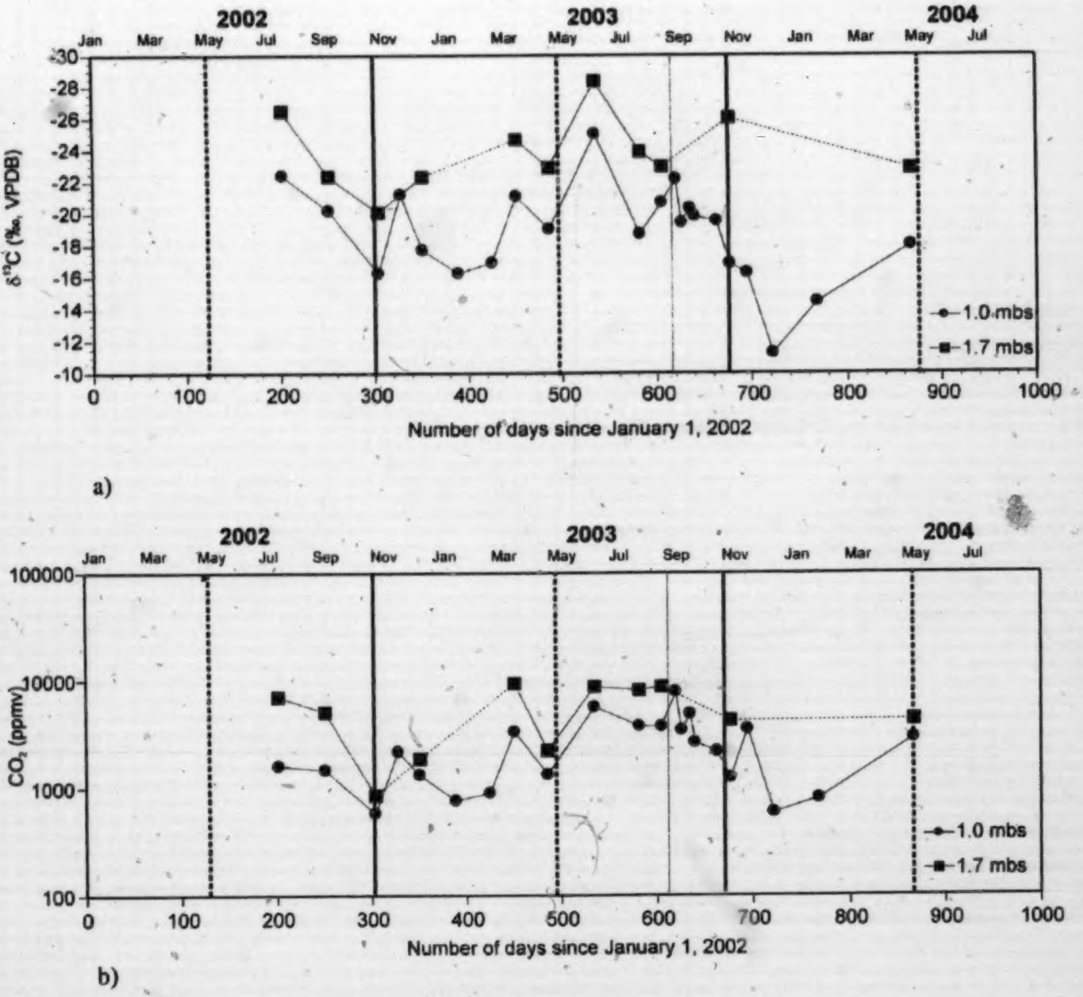

Figure 5-3 (a) Carbon stable isotopic compositions (‰, VPDB) and (b) CO_2 concentrations (ppmv) of soil gas samples collected at the background site at Edam.

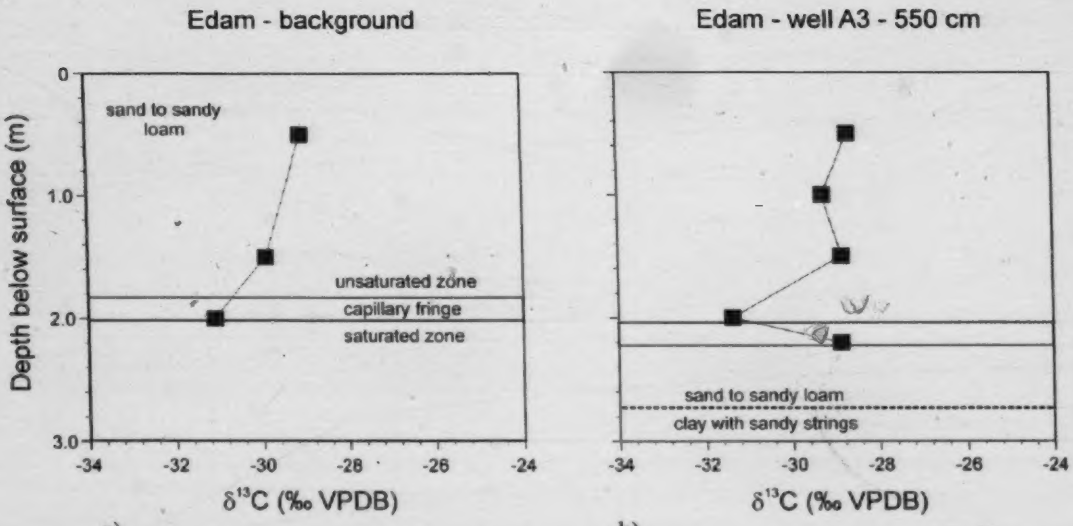

Figure 5-4 (a) Carbon stable isotopic composition of soil organic matter from the background site at Edam, and (b) in a profile 5.5 m away from well A3, Edam.

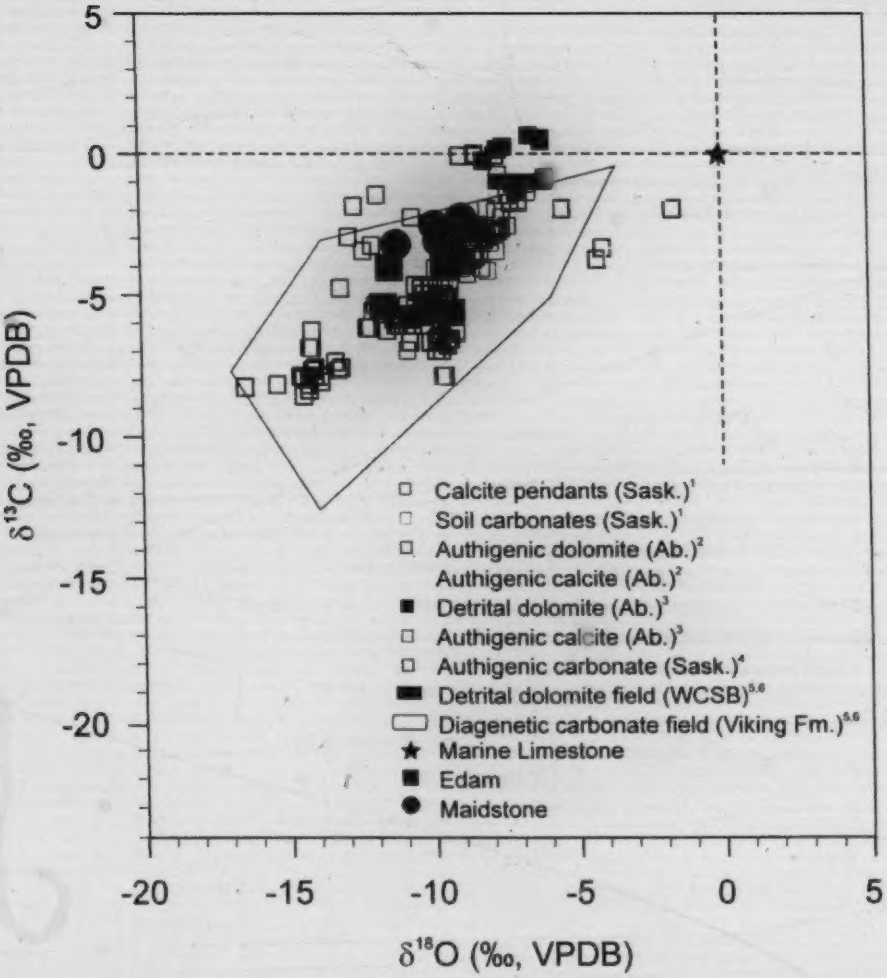

Figure 5-5 Carbonate samples from the saturated zone at Edam and Maidstone and detrital and authigenic soil carbonates from Saskatchewan and Alberta. Data from Landi (2000); Cohut *et al.*, (1995); Miller *et al.*, (1987); Cerling (1984). The "detrital dolomite" field reflects the $\delta^{18}O$ and $\delta^{13}C$ composition of detrital dolomite from the Upper cretaceous/Tertiary clastic sedimentary formations of the WCSB (Miller *et al.*, 1987; Longstaffe, 1987). The "diagenetic carbonate" field shows $\delta^{18}O$ and $\delta^{13}C$ values of diagenetic carbonates (calcite, siderite, ankerite, dolomite) from the Viking Formation (WCSB), modified by isotopic exchange with hot meteoric waters during the Laramide uplift and related fluid migration event in the basin (Longstaffe, 1987).

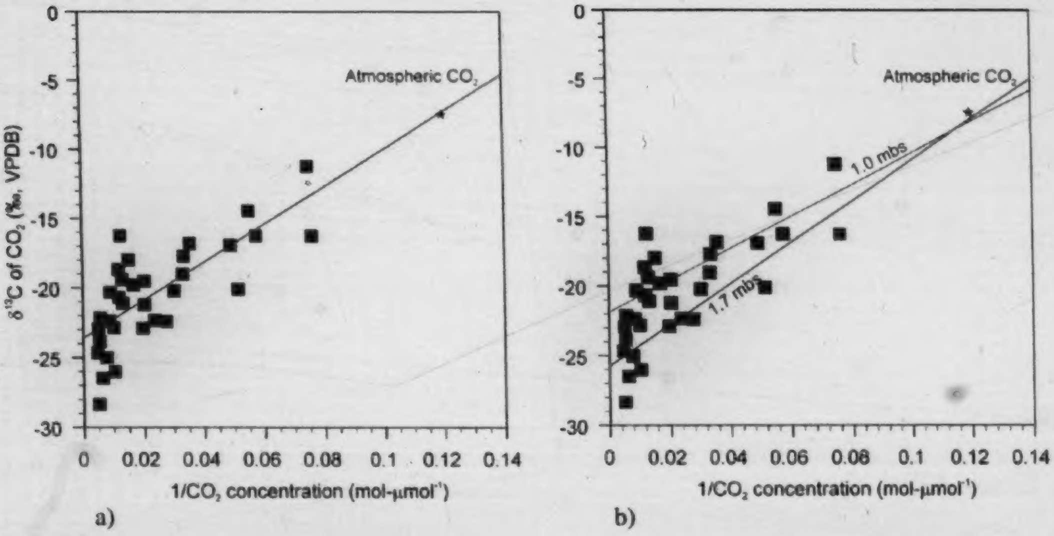

Figure 5-6 (a) Keeling plot of all background CO_2 samples collected at Edam. Best-fit line produces a lower intercept of -23.7 ‰, which is the average $\delta^{13}C$ of soil respired CO_2. (b) When samples collected at 1.0 mbs (light symbols) and 1.7 mbs (dark symbols) are plotted separately, it could be seen that shallow soil CO_2 has consistently higher $\delta^{13}C$ than deep soil CO_2. The two sets of data have intercept values of -22.5 ‰ (n=21) and -26.5 ‰ (n=11), respectively.

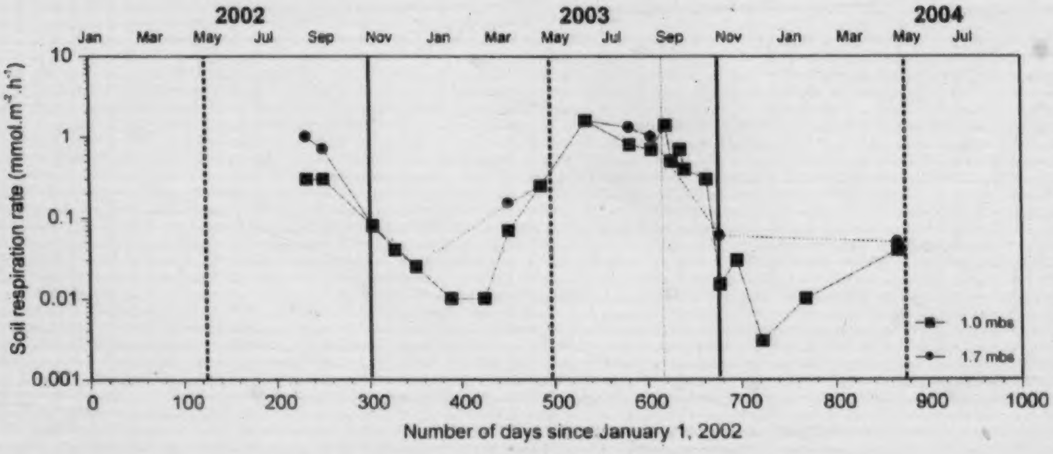

Figure 5-7 Soil respiration rates (mmol.m^{-2}.h^{-1}) calculated with the diffusion model using measured concentrations of soil CO_2 from samples collected at 1.0 and 1.7 mbs at the background site at Edam. The dashed lines on the graph connect points where analytical results from the deep probe are missing due to flooding and/or freezing of the probe. The vertical solid and dashed lines correspond to the onset of freezing and complete soil thawing, respectively.

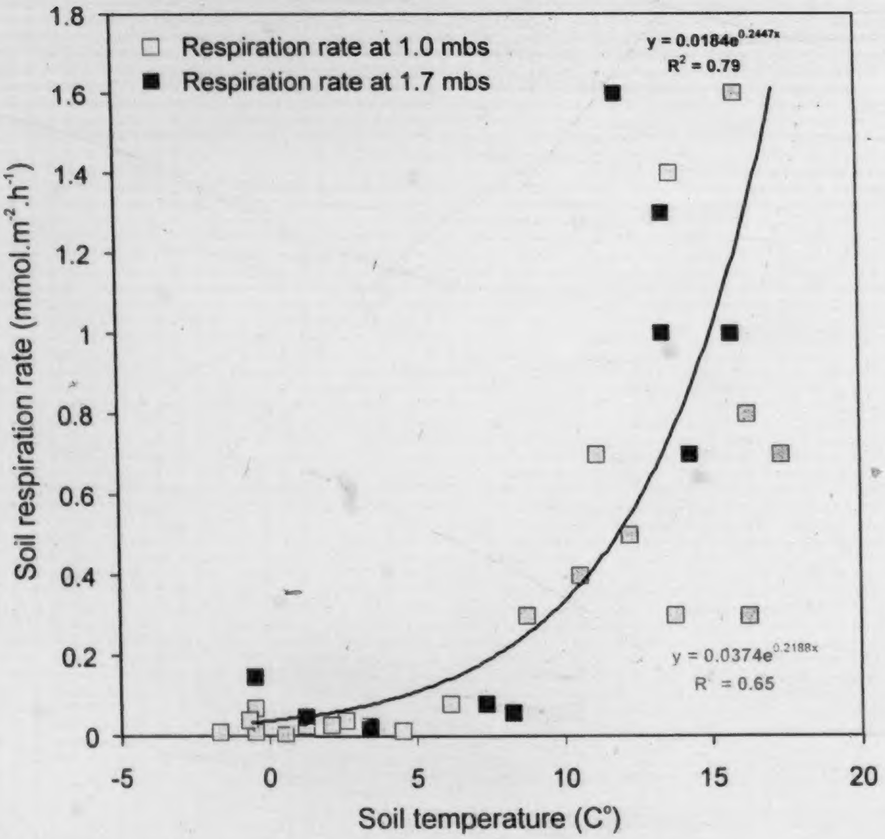

Figure 5-8 Estimated soil respiration rates (mmol.m^{-2}.h^{-1}) vs. soil temperature (^{o}C) at the background site near Edam, Saskatchewan.

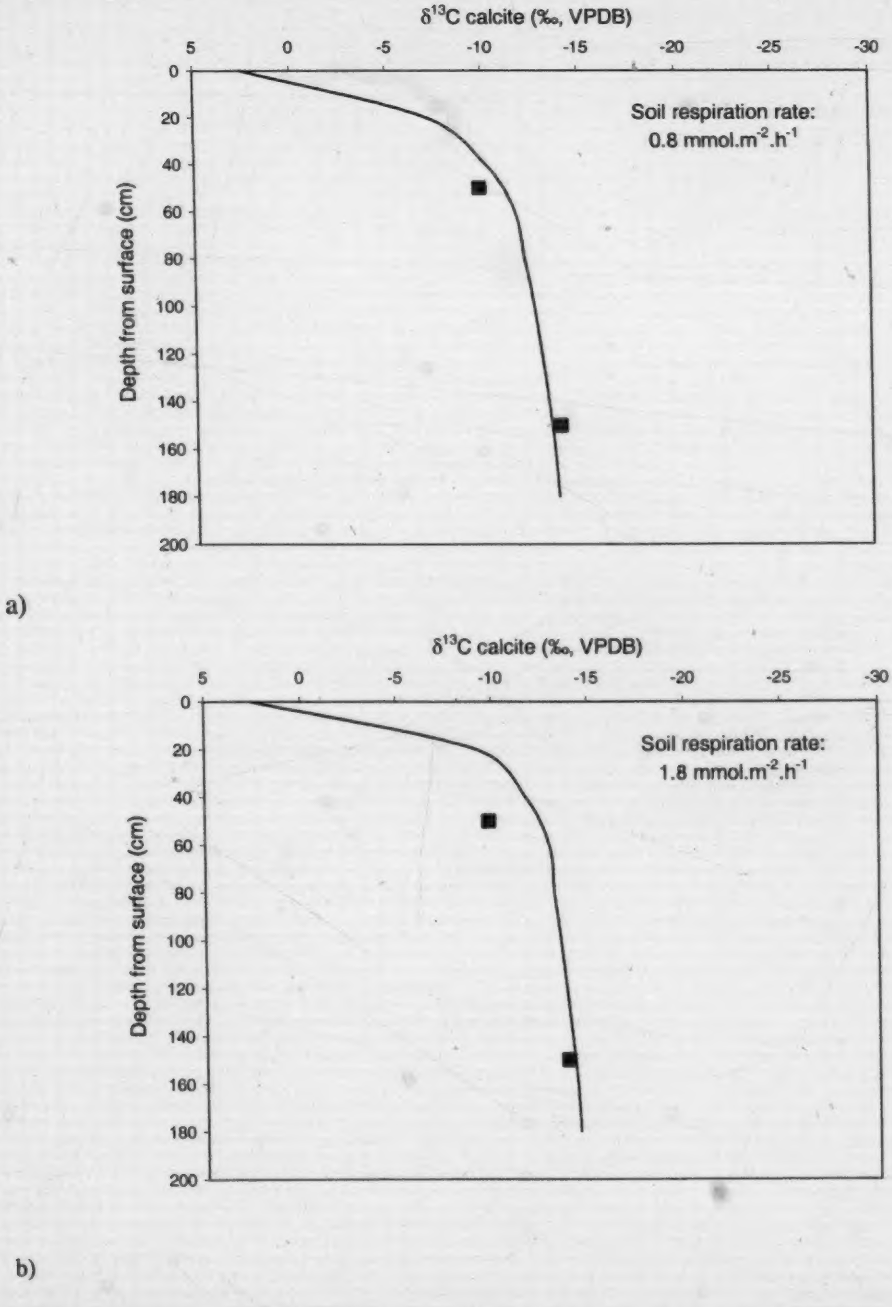

Figure 5-9 Model results vs. measured carbon isotopic compositions of bulk soil carbonate samples at the Edam background site at respiration rates of (a) 0.8 and 1.8 mmol.m^{-2}.h^{-1}. All other parameters and boundary conditions remain unchanged. Soil temperature in both cases is 15 °C.

Table 5-1 $\delta^{13}C$ composition, amount, and fraction of background soil carbonates from locations at Edam and Maidstone. The table also includes the $\delta^{13}C$ of SOM at Edam and pH of soil samples.

Date	Sample location (UWI)	Distance from well (m)	Depth (m)	$\delta^{13}C_{calcite}$ (‰,VPDB)	$\delta^{18}O_{calcite}$ (‰,VPDB)	$\delta^{18}O_{calcite}$ (‰,VSMOW)	Total calcite (mg/kg)	$\delta^{13}C_{SOM}$ (‰,PDB)	SOM amount (%)	soil pH
	EDAM (unsat.)									
18.06.2002	A4-17-048-19W3	100.0	0.5	-9.8	-8.5	22.1	25	-29.1	0.22	8.3
"	"	100.0	1.5	-13.9	-10.6	20.0	114	-29.9	0.21	7.5
"	"	100.0	2.0	-0.3	-5.9	24.9	15	-31.1	0.16	7.7
	EDAM (saturated)									
25.11.2001	A3-17-048-19W3	5.5	2.5	-4.0	-11.5	19.0	4500			8.8
		5.5	2.7							8.4
		5.5	3.0	-5.6	-9.4	21.1	33000			8.5
		5.5	4.0	-2.7	-8.6	21.9	46000			
		5.5	4.5	-3.1	-9.4	21.2	39000			
		5.5	5.0	-4.0	-9.6	20.9	45000			
		5.5	6.0	-5.4	-11.8	18.7	24000			
	MAIDSTONE (unsat.)									
25.06.2002	A10-11-048-23W3	19.0	0.5	-12.0	-13.8	16.7				8.0
"	"	22.0	0.5	-11.4	-5.3	25.2	1700			8.5
13.07.2001	B4-12-48-23W3	5.0	0.7				7300			7.7
28.08.2001	2C10-11-48-23W3	5.0	1.0	-3.3	-10.4	20.1	27000			8
"	"	30.0	1.0	-2.4	-9.4	21.2	15000			8.5
	MAIDSTONE (saturated)									
"	"	22.0	1.0	-3.3	-11.2	19.3	42000			8.8
"	"	22.0	1.5	-2.6	-9.9	20.6	17000			8.7
"	"	22.0	2.0	-3.1	-9.8	20.7	39000			8.6
"	"	22.0	3.5	-2.3	-9.0	21.5	45000			

Table 5-2 Concentration (ppmv) and carbon stable isotopic composition (‰, VPDB) of soil CO_2, collected at 1.0 and 1.7 mbs at the Edam background site from June 2002 to April 2004.

Date	$\delta^{13}C$ (‰, VPDB) 1.0 mbs	CO_2 ppmv 1.0 mbs	$\delta^{13}C$ (‰, VPDB) 1.7 mbs	CO_2 ppmv 1.7 mbs
18.06.2002	-18.07	6189	-18.60	9586
27.06.2002	-9.01	n.a.	-18.06	n.a.
11.07.2002	-18.78	3484	-18.07	n.a.
10.07.2002	-19.68	5147	-20.14	12349
21.07.2002	-22.41	1591	-26.49	7028
08.09.2002	-20.22	1464	-22.37	5086
31.10.2002	-16.28	579	-20.10	856
24.11.2002	-21.22	2161	n.m.	n.m.
17.12.2002	-17.73	1315	-22.33	1.858
24.01.2003	-16.27	765	n.m.	n.m.
01.03.2003	-16.93	897	n.m.	n.m.
27.03.2003	-21.10	3331	-24.68	9392
01.05.2003	-19.03	1327	-22.90	2233
19.06.2003	-25.02	5639	-28.36	8714
05.08.2003	-18.68	3730	-23.88	8069
28.08.2003	-20.68	3689	-22.95	8704
12.09.2003	-22.16	7751	n.m.	n.m.
18.09.2003	-19.40	3410	n.m.	n.m.
27.09.2003	-20.32	4854	n.m.	n.m.
02.10.2003	-19.80	2619	n.m.	n.m.
25.10.2003	-19.53	2161	n.m.	n.m.
08.11.2003	-16.83	1237	-26.02	4222
26.11.2003	-16.26	3494	n.m.	n.m.
23.12.2002	-11.23	588	n.m.	n.m.
07.01.2004	-14.45	798	n.m.	n.m.
16.04.2004	-17.99	2894	-22.85	4293

Table 5-3 Monthly and weighted average oxygen stable isotopic composition of local precipitation at Edmonton, Alberta and Wynyard, Saskatchewan (IAEA, WMO, 2001). These values were used to extrapolate average $\delta^{18}O$ compositions of soil moisture in west-central Saskatchewan.

Month	Edmonton	West Central Saskatchewan (est.)	Wynyard
January	-27.4	-28.6	-29.8
February	-26.1	-25.3	-24.5
March	-22.0	-22.0	-22.1
April	-20.9	-18.9	-16.8
May	-16.6	-13.2	-9.7
June	-13.7	-13.6	-13.4
July	-12.8	-13.0	-13.2
August	-15.4	-14.5	-13.7
September	-15.2	-14.9	-14.6
October	-16.2	-17.5	-18.9
November	-24.1	-22.7	-21.2
December	-28.7	-26.9	-25.1
Average	**-19.9**	**-19.2**	**-18.6**
Weighted Average	**-17.1**	**-16.3**	**-15.6**

Table 5-4 Oxygen isotopic compositions of soil CO_2 and the $\delta^{18}O$ of soil moisture (VSMOW) in isotopic equilibrium with the soil CO_2, at the respective soil temperatures measured at 1.0 and 1.7 mbs at Edam. Soil temperatures used to calculate $\delta^{18}O_{H2O}$ of samples at 0.2 cm were extrapolated from the data of Nichols (1998).

Date	UWI location	distance (m)	depth (mbs)	$\delta^{18}O_{CO2}$ (‰, VSMOW)	$\delta^{18}O_{H2O}$ in equilibrium (‰, VSMOW)
26.01.02	A3-17-049-19W3	0.2	1.0	33.3	-13.2
"	"	2.0	1.85	32.1	-14.5
06.05.02	A3-17-049-19W3	0.2	1.0	34.4	-12.1
"	"	2.0	1.85	31.5	-15.0
28.08.03	A3-17-049-19W3	0.2	0.2	27.6	-13.4
"	"	0.2	1.0	29.0	-13.7
"	"	0.2	1.85	28.5	-14.4
28.08.03	A4-17-049-19W3	0.2	0.2	28.1	-12.9
"	"	0.2	1.0	29.0	-13.8
25.10.03	A3-17-049-19W3	0.2	0.2	29.4	-15.6
"	"	0.2	1.0	30.8	-14.2
"	"	4.0	1.0	28.5	-16.4
"	"	0.2	1.85	29.1	-15.8
"	"	4.0	1.85	28.9	-16.0
23.12.03	A3-17-049-19W3	0.2	1.0	31.6	-14.9
"	"	4.0	1.85	28.6	-17.9
23.12.03	A4-17-049-19W3	0.2	1.0	27.2	-19.3
24.01.03	A3-17-049-19W3	0.2	1.0	36.0	-10.5
"	"	0.2	1.85	30.7	-15.9
24.01.03	A4-17-049-19W3	0.2	1.0	28.3	-18.2
07.02.04	A3-17-049-19W3	0.2	1.0	34.4	-12.1
"	"	0.2	1.85	33.6	-12.9
07.02.04	A4-17-049-19W3	0.2	0.2	22.7	-23.8
"	"	0.2	1.0	31.5	-15.0
04.03.04	A3-17-049-19W3	0.2	0.2	32.9	-13.6
"	"	0.2	1.0	31.4	-15.1
04.03.04	A4-17-049-19W3	0.2	1.0	26.2	-0.2.4
16.04.04	A3-17-049-19W3	0.2	0.2	23.9	-22.6
"	"	0.2	1.0	31.8	-14.7
"	"	0.2	1.0	33.0	-13.5
"	"	0.2	1.85	31.9	-14.6
"	"	4.0	1.85	31.3	-15.2
16.04.04	A4-17-049-19W3	0.2	1.0	25.8	-0.2.7
"	"	1.0	1.0	32.3	-14.2

Table 5-5 Oxygen isotopic composition of soil moisture and ground water at the Edam sites. The oxygen isotopic composition of soil moisture was measured on several soil samples collected at different dates. Ground water samples were collected from 2'' aluminum pipes installed at Edam to measure soil moisture with a neutron probe. The $\delta^{18}O$ of the soil water (‰, VSMOW) from the soil samples was corrected for gravimetric soil moisture content (see. McConnville *et al.*, 1999).

Date	Location and distance from wellhead (m)	Depth (m)	Sample type	$\delta^{18}O$ ‰ VSMOW	$\delta^{18}O$ ‰ VSMOW (corrected for soil moisture)
24.11.01	A3 at 5.5 m	0.5	soil moisture	-11.8	-12.5
“	“	1.0	“	-12.3	-12.7
“	“	1.5	“	-12.7	-12.8
“	“	2.5	“	-17.0	-17.0
24.11.01	A3 at 0.3 m	0.2	soil moisture	-16.7	-16.7
18.06.02	A3 at 100 m	0.2	soil moisture	-15.0	-15.0
07.01.04	A3 at 1.0 m	0.2	ground water	-13.4	n.a.
“	A3 at 4.0 m	0.2	“	-16.7	n.a.
“	A4 at 1.0 m	0.2	“	-16.2	n.a.

Chapter 6

Stable isotopic compositions and conditions of formation of soil carbonates near the leaking wells

Introduction

Natural seeps of liquid and gaseous hydrocarbons are found in a variety of marine and terrestrial environments. Authigenic carbonate minerals (e.g., calcite, Mg-calcite, aragonite) are common byproducts of the microbial oxidation of seeping hydrocarbons (Aloisi *et al.*, 2002; Donovan *et al.*, 1974; Schumacher, 1996). The $\delta^{13}C$ compositions of authigenic calcite and dolomite collected near marine and terrestrial hydrocarbon seeps are significantly lower than those of carbonates of marine, fresh water or pedogenic origin (Donovan *et al.*, 1974; Aloisi *et al.*, 2002). The low $\delta^{13}C$ result from the incorporation of carbon produced during the oxidation of gaseous and/or liquid hydrocarbons. The precipitation of carbonates related to the microbial oxidation of methane at the seafloor has been a common phenomenon through the geological history, as carbonate reefs composed of methane-derived calcite are found in sediments as old as the Neoproterozoic (Jiang *et al.*, 2003). Other authigenic minerals, such as pyrite, greigite, pyrrhotyte, and maghemite also form near hydrocarbon seeps (Schumacher, 1996). The precipitation of iron sulphides is attributed to bacterial sulphate reduction (Schumacher, 1996). Source of sulphur are H_2S gas or sulphur compounds in the oil and oil field water. Therefore, the close association of carbonates (calcite, Mg-calcite) with sulphide phases implies that mineral precipitation results from anaerobic oxidation of gaseous or liquid hydrocarbons (Aloisi *et al.*, 2002).

Authigenic soil carbonates are identified in samples collected in the soils near the leaking wells at Edam and Aberfeldy. SEM imaging reveals involvement of bacteria with the precipitation of some of these carbonates (Chapter 4). The participation of bacteria in calcite precipitation is either active or passive (Chapter 4). In the first case bacteria precipitates calcite as a metabolic byproduct

(Castanier *et al.*, 1999). Passive precipitation occurs when modifications in the local environment, such as rising carbonate alkalinity and/or pH occur due to bacterially mediated processes. As a result, bacteria may facilitate the precipitation and temporary preservation of carbonate minerals in environments where the physical and or chemical conditions are prohibitive of carbonate formation (Monger *et al.*, 1991; Oelssner *et al.*, 2003; Bosak and Newman, 2003; Aloisi *et al.*, 2002).

The principal objective of this chapter is to determine the factors that control the stable isotope composition of the two different types of authigenic soil carbonates near the leaking wells (Chapter 4). There are very few reports on the $\delta^{13}C$ and $\delta^{18}O$ compositions of bacteriogenic carbonates (e.g., Romanek *et al.*, 2000). Thus, the $\delta^{13}C$ and $\delta^{18}O$ of the abiotic and bacteriogenic calcites in the soil near the leaking wells are of particular interest, due to the information that those may provide on the nature of the biologically mediated processes and the timing of carbonate formation.

The $\delta^{18}O$ of paleosol calcite is often used as a paleoclimate indicator. Rates of abiotic calcite precipitation in soils are slow and imply isotope equilibrium (Cerling, 1984). Bacterial precipitation of calcite, however, could be a rapid process and thus kinetic disequilibrium effects are possible. Clarification on the nature (e.g., equilibrium vs. disequilibrium) of bacterially mediated calcite precipitation is of particular importance to studies that utilize the isotopic composition of authigenic soil carbonates to reconstruct past climate conditions.

Results

Stable isotope compositions and amount of soil carbonates

A total of 89 bulk soil and selected calcite[4] samples collected in soil near the leaking wells are analyzed for $\delta^{13}C$ and $\delta^{18}O$. The $\delta^{13}C$ and $\delta^{18}O$ values of these samples vary from -0.2 to -57.6 ‰ and from -3.6 to -22.1 ‰ (VPDB), respectively (Appendix 4). Soil carbonates collected in microaerophilic soil near the wells have the lowest $\delta^{13}C$ and $\delta^{18}O$ values. The amount of carbonate (calcite) in the bulk soil samples varies widely from as little as 3 mg/kg to as much as 50000 mg/kg. The lowest amounts are measured in the sandy soil at Edam, whereas the clayey loam at Aberfeldy contains the highest amounts of carbonate. Results are presented in Appendix 4, Figures 6-1 to 6-3.

Edam research site

Soil samples were collected and analyzed for $\delta^{13}C$ and $\delta^{18}O$ at four wells from the Edam field (e.g., A3, A4, A10-36-48-23W3, and 14C-28-048-19W3). Most samples, however, were collected at different depths and distances around wells A3 and A4. Most bulk soil samples collected in microaerophilic soil at well A3 have $\delta^{13}C$ lower than -25 ‰, with values as low as -57.2 ‰. Samples of authigenic calcite selected from bulk soil samples collected at 0.3 m distance from the well casing have similar low $\delta^{13}C$ compositions (e.g., -57.6 to -55.1 ‰). One selected sample at 2.0 mbs and 2.0 m distance form the well has higher $\delta^{13}C$ of -31.7 ‰. Bulk samples at well A4 also have low $\delta^{13}C$ (e.g., -35.0 to -53.0 ‰; Appendix 4). Bulk soil samples collected near well C14-28-048-19W3M have $\delta^{13}C$ values close to those of pedogenic carbonates in Saskatchewan (Landi, 2002). The $\delta^{13}C$ of bulk soil samples form the oxygen-rich soil at Edam vary from -2.7 to -19.9 ‰ with an average value of -11.0 ‰. Most carbonates from the oxygen-rich soil have $\delta^{13}C$ values similar to those of background soil carbonates.

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[4] EDS and XRD demonstrates that calcite is the predominant carbonate in soil samples (Chapter 4).

The $\delta^{18}O$ compositions of samples from microaerophilic soil near wells A3 and A4 vary from -11.0 to -22.0 ‰ with an average value of -16.0 ‰. There is a difference in the $\delta^{18}O$ of bulk soil carbonate samples in the microaerophilic soil between the two wells. The average $\delta^{18}O$ value at A4 is -18.2 ‰ with the lowest value of -22.0 ‰, whereas the average $\delta^{18}O$ at well A3 is -15.5 ‰ with the lowest value of -18.8 ‰. Selected calcite samples near well A3 have $\delta^{18}O$ compositions that vary between -16.9 and -20.0 ‰. The $\delta^{18}O$ of bulk soil samples from the O_2-rich soil near wells A3 and A4 vary from -7.0 to -19.0 ‰ with an average value of -14.1 ‰. The $\delta^{18}O$ of bulk soil samples collected near well 14C-28-048-19W3 are significantly higher and fall within the range of values typical for background carbonates (Chapter 5; Appendix 4).

The amounts of soil carbonate in the bulk samples from the microaerophilic soil at well A3 vary by two orders of magnitude (e.g., from 10 to 1200 mg/kg). The highest amounts of soil carbonate are measured in samples collected in the immediate vicinity of the well. Significant variability precludes estimates of average soil carbonate contents. The highest soil carbonate content near well A4 is also measured in soil near the well (e.g., in microaerophilic soil). Variability at this site is significant too (Table 5-1). A change in soil lithology from fine-grained sand and sandy loam to clayey loam at 1.5 mbs is accompanied by a three orders of magnitude increase in the soil carbonate content (Appendix 4). Similar high carbonate content (16000 mg/kg) is estimated for a clayey loam sample at well C14-28-048-19W3M (Appendix 4). Soil samples collected from the oxygen-rich soils at the Edam sites have low uniform carbonate contents (e.g., 150-250 mg/kg). In contrast, sandy loam/gravel at well A10-36-048-023W3M contains as much as 6300 mg/kg of carbonate.

Maidstone research site

Samples collected in the microaerophilic soil near well A10 at Maidstone have $\delta^{13}C$ compositions that vary from -21 to -1.0 ‰ with an average value of -8.8 ‰. Samples from the O_2-rich soil have lower average $\delta^{13}C$ (e.g., -4.7 ± 2 ‰) and exhibit less variability. The $\delta^{18}O$ of samples collected in the microaerophilic soil vary from -3.6 to -16.6 ‰. The $\delta^{18}O$ of samples in the oxygen-rich soil is less variable (e.g., from -14.2 to -9.4 ‰). The clayey loam in the microaerophilic zone near this well has homogeneous soil carbonate content (e.g., from 19000 mg/kg near the wellhead to 12000 g/kg at 12.0 m). In contrast, background soil at the same depth contains two to four times more carbonate (Appendix 4). Carbonate concentrations in the sand and gravel at 0.5 mbs vary from 7000 to 12000 mg/kg. Oxygen-rich soil in the upper parts of the sand/gravel cover contains between 1000 and 9000 g/kg carbonate (Appendix 4). The soil carbonate content of samples collected near the rest of the Maidstone wells varies from 8000 to 46000 mg/kg.

Aberfeldy well sites

Aberfeldy samples are divided into three groups. The first group includes two bulk soil samples collected in microaerophilic soil near the wells. These samples have $\delta^{13}C$ compositions of -6.6 to -17.4 ‰ respectively. The second group consists of carbonate (calcite) crusts collected from the casings of the wells. The crusts consist of calcite, iron hydroxides, and a variety of detrital minerals, such as clays, feldspars and micas (Chapter 4). The $\delta^{13}C$ of these samples varies from -24.7 to -45.8 ‰. The third group consists of calcite samples selected from the carbonate crust samples.

As mentioned, the $\delta^{13}C$ compositions of the two bulk samples collected above and below the LDPE hood of the gas-capturing device at well A9-17-049-26W3 differ by 12 ‰ (Appendix 4). The sample collected within the hood has lower $\delta^{13}C$. The large difference indicates that carbon sources above and below the hood are different. There is also a significant difference in the total carbonate content of the two bulk soil samples (Appendix 4). The sample collected above the LDPE hood contains 25000 mg/kg carbonate, whereas the carbonate content of the sample at 2.46 mbs (below the hood) is two times higher (e.g., 49000 mg/kg). No difference in the carbon stable isotope composition was observed at well C8-17-049-26W3, however, where samples were also collected above and within the hood.

The oxygen isotope composition of the two bulk soil samples collected in microaerophilic soil at well A9-17-049-26W3 is similar (e.g., ca. -11 ‰). The bulk carbonate crusts and selected calcite samples from the microaerophilic soil have lower $\delta^{18}O$ compositions that vary from -12 to -17 ‰. It is worth noting that the $\delta^{18}O$ compositions of selected calcite samples at Aberfeldy are as much as one permil higher than those of the bulk samples the selected samples were picked from (Appendix 4), even though in most cases the selected samples had lower $\delta^{13}C$ compositions.

Carbon stable isotope composition and amounts of soil organic matter (SOM)

The $\delta^{13}C$ of soil organic matter (SOM) was measured on 49 samples collected around wells A3 and A4 in the background location at Edam. Out of those 49 samples 38 are bulk samples and 11 are selected samples (Appendix 4). The $\delta^{13}C$ of the samples around the well sites varies from -24.2 to -48.8 ‰ with the lowest $\delta^{13}C$ values measured in soil samples collected close to the well bore and soil surface. The analysis of selected samples did not produce low $\delta^{13}C$ values, as it was observed with calcite. On the contrary, selected SOM samples have the same or higher values than the bulk samples.

The amount of soil organic matter in the microaerophilic soil at Edam varies from 0.2 to 0.5 weight percent. Higher concentrations are measured in the vicinity of well A3, immediately close to well bore at 2.0 mbs. In oxygen-rich soil organic carbon varies from 0.1 to 0.6 % with the highest values measured in a sample collected ca. 2.0 m away from well A4 (Appendix 4).

Soil pH

Soil pH at the majority of the wells increases significantly with depth and/or proximity to the source of leakage (Appendix 4; Fig. 6-4). Elevated soil pH values are also measured where liquid hydrocarbon contamination is located. For example, the highest pH values at well A10 are measured in samples that contain free product (e.g., heavy oil). In both cases, the O_2 and CO_2 concentrations in soil gas in these domains are low (Chapter 3).

Discussion

The highly variable stable isotopic compositions of soil carbonates from the microaerophilic and soils suggest that soil type, oil contamination, and the dominant mechanisms of carbonate precipitation (e.g., abiogenic vs. bacteriogenic) play important roles in the formation and/or preservation of the carbonate minerals. Low $\delta^{13}C$ values at Edam and Aberfeldy demonstrate the incorporation of carbon derived from the oxidation of methane. The range of $\delta^{13}C$ compositions of the soil carbonates at Maidstone is consistent with the incorporation of heavy oil or C_3 plant-derived carbon. The low $\delta^{18}O$ of most selected calcite samples and some bulk soil carbonates from the microaerophilic and oxygen-rich sandy soils at Edam are unique, however, as such values have not been reported to date in Saskatchewan and/or Alberta.

SEM imaging suggests that the precipitation of calcite along the casings of the Aberfeldy wells is an inorganic process (Chapter 4). Therefore, the $\delta^{13}C$ and $\delta^{18}O$ compositions of selected and bulk carbonate crust samples collected at Aberfeldy should be representative for those of abiotic soil carbonates. The $\delta^{13}C$ and $\delta^{18}O$ compositions of selected carbonate samples collected in soil at well A3 at Edam overlap at 0.5 mbs indicating that all carbonate at this depth is of authigenic origin. SEM imaging demonstrates that calcite identified in these samples is of bacteriogenic origin (Chapter 4). Therefore, the $\delta^{13}C$ and $\delta^{18}O$ compositions of selected samples near well A3 likely reflect the stable isotope composition of bacteriogenic calcite at the sites. Samples from the microaerophilic soil at Maidstone were not examined by SEM, and it is, thus, not known if carbonate precipitation at this site is inorganic or bacterially mediated. SEM imaging of a carbonate pendant collected from the O_2-rich soil near the well reveal textures similar to those of bacteriogenic calcites at Edam.

Amounts and rates of authigenic carbonate precipitation

To better understand the processes related to calcite precipitation (and dissolution) in soil near the leaking wells, it is important to know the compositions and proportions of soil carbonates of different origin. The stable isotope composition of authigenic carbona[illegible]dam is determined by analyzing minute amounts of calcite separated from bulk soil and carbonate crust samples (Chapter 2). Although no selected carbonates samples were collected at well A4, the nearly identical $\delta^{13}C$ of soil CO_2 at the two wells indicates that authigenic carbonates at well A4 should have $\delta^{13}C$ compositions similar to those at well A3. Therefore, the $\delta^{13}C$ compositions of the selected carbonate samples collected at well A3 are also used to calculate the amount of authigenic carbonate at well A4.

The $\delta^{18}O$ and $\delta^{13}C$ compositions of authigenic calcite are also estimated by calculating a range of possible $\delta^{13}C$ and $\delta^{18}O$ values of calcites that can form in isotopic equilibrium with soil CO_2 produced during the oxidation of natural gas and heavy oil at the monitoring sites. This method is also used at Edam to verify the authigenic origin of selected calcite samples and to constrain the timing of carbonate precipitation. Although long-term monitoring data are available, the lack of selected calcite samples from the microaerophilic soil at Maidstone renders estimates of the isotope compositions of authigenic calcite at this site uncertain. The low $\delta^{18}O$ values of few bulk soil samples at Maidstone, however, suggest that those are close to isotopic equilibrium with local soil H_2O, and hence consist of close to 100 % authigenic carbonate.

Edam research site

The highest amount of authigenic carbonate in the microaerophilic soil near well A3 is estimated from a sample collected at 1.5 mbs, and 0.3 m away from well bore, whereas the lowest is measured in a sample collected at 2.0 mbs and 4.0 m away from the well (Appendix 4). The high amount of authigenic carbonate at 1.5 m coincides with the highest soil pH value measured around the wells (Appendix 4). Soil at 2.0 m distance from this well contains less total authigenic carbonate likely due to the detrimental effects of low pH related to the high amounts of soil CO_2 produced from the aerobic oxidation of CH_4. The estimated amount of authigenic carbonate in the sandy portion of the microaerophilic soil at this well (i.e., 0.5 to 1.0 mbs) varies from 86 mg/kg to 490 mg/kg. In contrast, the estimated amount of authigenic carbonate in the clayey loam at 1.5 mbs reaches ca. 42000 mg/kg, which is the highest estimated amount of authigenic soil carbonate at the Edam well sites.

In spite of the presence of significant quantities of low $\delta^{13}C$ CO_2, soil carbonates in oxygen-rich soils near the wells do not contain methane-derived carbon (Chapter 3). Exceptions are a few samples at well A4 that have $\delta^{13}C$ compositions indicative of the presence of minor amounts of methane-derived carbon. Monitoring demonstrates that little methane-derived CO_2 was available in the oxygen-rich soil away from this well, in the past two years (Chapter 3). A comparison of the $\delta^{13}C$ of soil CO_2 in the O_2-rich soil at this site with the $\delta^{13}C$ of soil CO_2 collected at the background site reveals that the presence of methane-generated CO_2 in these parts of the soil at well A4 is noticeable only in winter. Therefore, the low $\delta^{13}C$ soil carbonates likely formed prior to the installation of the soil gas probes, when leaking gas rates at this well may have been higher. Alternatively, those carbonates formed from soil CO_2 produced from the oxidation of bacteriogenic CH_4 generated in the soil or in the shallow aquifer at the site.

Rates of authigenic calcite precipitation in arid, non-agricultural soils are estimated to be ca. 0.5 to 4.5 $mg.kg^{-1}.y^{-1}$ (Cerling, 1984). The estimated rates of authigenic soil carbonate precipitation at the two monitoring sites at Edam are between one and two orders of magnitude higher. The estimated rates of authigenic carbonate formation in the clayey portion of the soil near well A4 are even higher (i.e., ca. one order of magnitude) than these estimated in sandy soil (Appendix 4).

Maidstone research site

The amounts and stable isotope compositions of soil carbonates collected near well A10 are significantly different to those at Edam (Table 1-6; Fig. 6-3). With the exception of one sample collected 6.0 m away from the well, the total carbonate content of the oxygen-rich soils is lower than the carbonate content of the microaerophilic soils. This is related to the more oxidizing conditions favorable of calcite dissolution, as suggested by the lower soil pH (Appendix 4). The higher amount of total soil carbonate is apparently related to the presence of detrital and/or pedogenic carbonate in the soil. Well A10 was drilled 41 years ago (IHS Energy™, 2001). If the oil spill at this site occurred close to that time, and if carbonatogenesis at the site were related to the spill, it is estimated that about 300 mg.kg^{-1} of new authigenic carbonate formed in the soil near the well every year since. This is two times the rate estimated from sandy soils at Edam, but still one order of magnitude lower than the rate of authigenic calcite growth in the clayey soil near well A4.

Supplies of dissolved calcium and bicarbonate are the two major rate-limiting factors for authigenic soil calcite precipitation (Lal and Kimble, 2000). Precipitation of authigenic soil calcite is considered a poor sink for organically respired carbon, because of limitations to the Ca^{2+} and/or Mg^{2+} supplies (Monger and Gallegos, 2000). Calcium is supplied by the dissolution of detrital or authigenic carbonate, by the alteration of silicate minerals in the upper parts of the soil profile, and by rainwater and atmospheric dust transport (Monger, 2002). The estimated amount of authigenic carbonate in soils near the wells correlates only with the total amount of soil carbonate. This correlation indicates that the amount of Ca^{2+} of calcite origin is the major limiting factor on the amount of hydrocarbon-derived carbon trapped in the form of soil carbonate. Therefore, despite the high production rates, significant amounts of hydrocarbon-derived carbon are not trapped as authigenic carbonate in the soil near the wells. Instead, authigenic calcite in soil near the wells appears to be recycled in series of dissolution and re-precipitation reactions driven by seasonal changes in soil P_{CO2}, temperature and moisture.

Conditions and timing of calcite precipitation

Edam research site

Most soil carbonate samples collected from the microaerophilic and oxygen-rich soils at Edam have $\delta^{18}O$ compositions significantly lower than those of background soil carbonates (Fig. 6-5). In addition, the $\delta^{18}O$ compositions of authigenic calcites at Edam are as much as 5 ‰ lower than the lowest $\delta^{18}O$ of abiotic authigenic carbonates at Aberfeldy and/or Maidstone (Fig. 6-3). The isotope composition of soil carbonate samples (bulk and selected) collected from the microaerophilic and oxygen-rich soils near the wells are compared to the $\delta^{18}O$ and $\delta^{13}C$ compositions of hypothetic calcite that would precipitate in equilibrium with soil moisture and soil CO_2 through the year. The comparison reveals that a number of samples have $\delta^{18}O$ compositions apparently incompatible with equilibrium precipitation (Fig. 6-6).

If equilibrium precipitation is assumed, calcite in the soil near the two wells should have precipitated from CO_2 having $\delta^{13}C$ of ca. -67 ‰. Two years of soil gas composition monitoring at the well sites demonstrate that soil CO_2 with this composition is produced only in May and November, when soil temperature is between 2 and 4°C. Soil water in equilibrium with authigenic calcite within the above temperature range should have $\delta^{18}O$ compositions that vary between -21 and -23 ‰ (VSMOW). The $\delta^{18}O$ compositions of soil carbonates near well A4, however, (e.g., -22.1 ‰) indicate that waters having $\delta^{18}O$ as low as -25 ‰ (VSMOW) should have been involved in the precipitation of authigenic calcite. Mass balance calculations (not included) reveal that soil waters having $\delta^{18}O$ as low as -25 ‰ consist of 80 % winter precipitation. Although the $\delta^{18}O$ values of soil moisture measured in winter/early spring near well A4 demonstrate that winter precipitation percolates down into the soil profile near wells A3 and A4 in spring (Chapter 5), the $\delta^{18}O$ of these waters is 2 to 3 ‰ too high to explain the observed low $\delta^{18}O$ compositions of the soil carbonates. Monitoring of the $\delta^{18}O$ of soil water near the wells, however, postdates soil calcite precipitation and, for the most part, coincides with a period of drought in Western Canada (e.g., 2001-2002; Wheaton *et al.*, 2005). Therefore, it is possible that soil water of $\delta^{18}O$ composition lower than that measured during the monitoring period was present in soil during the precipitation of bacteriogenic calcite.

If soil calcite precipitated in equilibrium with local moisture and CO_2 at the estimated low soil temperatures, low $\delta^{13}C$ of soil CO_2 and low $\delta^{18}O$ of soil water suggest mineral formation within a very narrow time period. This period starts at the end of April, immediately after the ice/frost layer in shallow soil thaws and allows winter precipitation to infiltrate the sandy soil. Calcite precipitation should, therefore, end prior to the end of May when high $\delta^{18}O$ precipitation would displace the low $\delta^{18}O$ soil water, and evaporation related to rising soil temperatures would enrich further soil moisture in ^{18}O. Equilibrium precipitation in late spring requires a substantial snow cover that would prevent the development of a thick ice layer in the soil. Moderate temperatures in April/May are also required to prevent extensive evaporation and to keep soil moisture content high. Although inorganic growth of authigenic calcite would not be favored at high water saturation (Cerling, 1984; Stern *et al.*, 1994; Tabor *et al.*, 2002), it should not be a limiting factor if calcite precipitation is mediated by bacteria. Thus, the low $\delta^{18}O$ composition of soil calcite could be used as another line of evidence for bacteriogenic origin.

The $\delta^{18}O$ composition of soil carbonates near the leaking wells at Edam is significantly lower than that of soil carbonates collected near the rest of the leaking wells, and also than that of the 180+ soil carbonate samples from Saskatchewan and Alberta (Landi, 2002; Chapter 5). As mentioned above, few soil carbonate samples collected from oxygen-rich soils further away from the wells also exhibit similar low $\delta^{18}O$ compositions, and thus may also be of bacteriogenic origin (Table 1-6). The lack of similar, low $\delta^{18}O$ values in the large group of published soil carbonate data suggests that either bacterially mediated precipitation of soil calcite is rare or that the $\delta^{18}O$ composition of bacteriogenic calcite is modified by subsequent dissolution and re-precipitation. Dissolution and re-precipitation of soil carbonates is a common phenomenon related to the re-distribution of carbonate in the soil column (Monger, 2002). In contrast to bacteriogenic precipitation, those processes are driven in part by decreasing soil moisture; therefore, exchange with evaporated soil water will obliterate the low primary $\delta^{18}O$ compositions of bacteriogenic calcites. The latter explains the predominance of pedogenic carbonates that have $\delta^{18}O$ compositions close to equilibrium with the weighted average annual $\delta^{18}O$ of the precipitation in the respective areas (Cerling, 1984).

Maidstone research site

Soil carbonate samples at well A10 can be divided into two groups (Fig. 6-7). The first group includes bulk samples collected from the microaerophilic and oxygen-rich soil at distances from the well that vary from 1.0 to 12.0 m. The comparatively low $\delta^{18}O$ of two samples from this group is similar to the low $\delta^{18}O$ values of pendants collected in pristine non-agricultural soils from the Gray soil belt of Saskatchewan (Landi, 2002), and suggest that the former consist of nearly pure authigenic carbonate. The $\delta^{18}O$ of the two Maidstone samples is in isotope equilibrium with soil water that has $\delta^{18}O$ of -18 ‰ (VSMOW). Although this is ca. 2 ‰ lower than the $\delta^{18}O$ of the weighted average precipitation in the area, it is nevertheless similar to the estimated $\delta^{18}O$ of water in equilibrium with abiotic calcite at Aberfeldy, suggesting similar conditions during authigenic calcite precipitation. Shallow (1.0 m) clayey soils near Edmonton, Alberta also contain soil water of similar $\delta^{18}O$ (Maule *et al.*, 1994). The $\delta^{13}C$ of these two samples are in isotope equilibrium with a hypothetical soil CO_2 that has $\delta^{13}C$ of -18.5 ‰. Therefore, the $\delta^{13}C$ of precursor organic matter or heavy oil should be ca. -23 ‰ (Cerling, 1984; Chapter 5). The $\delta^{13}C$ of heavy oil in Western Canada, however, is ca. -30 ‰ (Ringham, 1986), whereas the average $\delta^{13}C$ of SOM in the Gray soil zone in Saskatchewan, where the leaking well sites are located, is -26.5 ‰ (Landi, 2002). The latter number is similar to this estimated for SOM at the background site at Maidstone (i.e., -27.4 ‰; Chapter 5). Although enrichment of residual hydrocarbons with $\delta^{13}C$ is possible during the aerobic/anaerobic oxidation of oil, it seems unlikely because the heavy Mannville oil is already significantly biodegraded (Dimitracopoulus and Muehlenbachs, 1986). Methanogenesis is the second important microbial process at this well site (Chapter 3). Therefore, a fraction of the soil CO_2 in equilibrium with authigenic soil carbonate is likely produced from methanogenesis. The $\delta^{13}C$ CO_2 compositions measured during the monitoring period at this site suggest that the fraction of methanogenic CO_2 was larger in the past.

The second group consists of samples collected in the immediate vicinity of the well. The $\delta^{13}C$ of these samples varies from -3.3 to -21.3 ‰ (Table 1-6). The sample with the lowest $\delta^{13}C$ formed in equilibrium with CO_2 having $\delta^{13}C$ of -32 ‰, indicating the involvement of minor amounts of methane-derived carbon. The very high $\delta^{18}O$ composition of the only selected sample collected at 0.2 mbs indicates that it formed during extensive evaporation. Most soil carbonate samples collected at the rest of the Maidstone wells have carbon and oxygen isotope compositions similar to those of samples collected close to the casing of well A10 (Fig. 6-8).

Aberfeldy well sites

Lack of molecular and stable isotope composition data of soil gases at Aberfeldy does not allow the timing of authigenic carbonate precipitation to be determined. By assuming an average soil temperature of 7°C (Chapter 3), authigenic soil calcite at Aberfeldy should have precipitated in equilibrium with CO_2 of $\delta^{13}C$ between -58 and -60 ‰. This range of $\delta^{13}C$ values is too high for CO_2 to be of methane origin alone and should, therefore, include CO_2 produced from the oxidation of heavy oil or from methanogenesis. At 7°C (assumed to be the average annual soil temperature) the $\delta^{18}O$ of authigenic calcite at Aberfeldy is in isotope equilibrium with soil water of ca. -20 ‰ (VSMOW). This value is lower than the estimated average annual precipitation in the area, which indicates that at the time of carbonate precipitation, soil water contained a significant fraction of winter precipitation. Therefore, abiotic calcite likely precipitated sometimes between late fall and late spring.

Inorganic calcite precipitation and the distribution of abiotic calcite

Field observations, SEM imaging, and stable isotopic analysis demonstrate that abiotic calcite is absent from the shallow soils at Edam (e.g. <0.1mbs), in the gravel zone at well A10, and in the shallow sections (0.7-1.0 mbs) of the well bore casings at Aberfeldy. In fact, abiotic calcite at well A3 at Edam is only detected by SEM in a sample at 1.5 mbs where conditions are microaerophilic (e.g.,

O_2<1.0 % v/v; Chapter 3) and pH is high (Fig. 6-4). Inorganic precipitation of calcite depends on the availability and concentration of Ca^{2+} and HCO_3, the pH of the medium, and the availability of nucleation sites (Hammer and Verstraete, 2002). The following carbonate equilibrium reactions reflect the processes related to the dissolution and precipitation of authigenic calcite in soil (Lal and Kimble, 2000):

$$CO_2+H_2O \leftrightarrow H^+ + HCO_3^- \leftrightarrow H_2CO_3 \quad [6\text{-}1]$$

$$CaCO_3+H_2CO_3 \leftrightarrow Ca^{2+}+2HCO_3^- \quad [6\text{-}2]$$

The second reaction moves to the left (carbonate precipitation) if P_{CO2} drops, or the pH of soil solution rises. Calcite precipitation may also be triggered by loss of water from the soil solution due to evaporation or evapotranspiration, or by mixing of two solutions with different compositions. Of these, drop of P_{CO2} and water loss through evaporation are the mechanisms likely to play major roles for inorganic precipitation of authigenic carbonate in soils near the leaking wells.

Carbon dioxide in soils near the leaking wells is supplied by the bacterial oxidation of gaseous and/or liquid hydrocarbons (Chapter 3). However, elevated soil CO_2 concentrations also cause a drop in the pH of the ambient solution especially in the absence of suitable proton acceptor(s) (cf. Bennet and Rogers, 2001; Valentine, 2002). The clayey soils at Aberfeldy and Maidstone contain detrital carbonates that have the capacity to buffer the pH of the soil solutions. The sandy soils at Edam and the gravel cover at well A10 at Maidstone, however, contain little or no detrital carbonate and are thus vulnerable to carbonic acid attacks. Soil solution in equilibrium with soil carbonate and atmospheric air has a pH value of 8.4 (Pal *et al.*, 2000). With the exception of two samples near well A3, however, areas of high soil CO_2 concentrations near the leaking wells have lower pH values (e.g., from 7.6 to 5.5; Fig. 6-4). Therefore, detrital and/or pedogenic soil carbonates from the upper parts of the soil or the leaky well casing are dissolved by the influx of rain and/or ice/snow melt water carrying dissolved CO_2 produced from the bacterial oxidation of hydrocarbons. The ensuing solution migrates downwards where calcite precipitates either due to evaporation or upon reaching domains where CO_2 content is low and/or the soil contains enough proton acceptors capable of buffering the pH. Similar "washing out" and re-precipitation of soil carbonates is observed in semi-arid soils (Nordt *et al.*, 2000) where it leads to the formation of distinct petrocalcic horizons (Lal and Kimble, 2000).

Mechanisms of bacteriogenic carbonate precipitation near the leaking wells

Bacteria mediate calcite precipitation by increasing the alkalinity of the medium through a variety of physiological processes (Fujita *et al.*, 2000; Hammes and Verstraete, 2002). Elevated soil pH measurements demonstrate that processes other that methanotrophy occur in soils near the leaking and contaminated wells. Several bacterially mediated processes that can elevate alkalinity and/or pH in soils and most of those have been associated with bacterially mediated precipitation of soil carbonates. Most processes are mediated by anaerobic bacteria, whereas others are mediated by both aerobic and anaerobic microorganisms. One of the best-studied processes is the production of ammonia (NH_4^+) from the hydrolysis of urea by heterotrophic bacteria (Rivadeneyra *et al.*, 1998; Fujita *et al.*, 2000; Hammes *et al.*, 2003) according to the reaction:

$$H_2NCONH_2 + 2H_2O + Ca_2^{+} \leftrightarrow 2NH_4^{+} + CaCO_3 \quad [6\text{-}3]$$

Both aerobic and anaerobic bacteria mediate the process. Lab culture experiments of calcite precipitation involving urea hydrolysis by isolates of *B. Pasteurii* by Fujita *et al.*, (2000) show an increase of pH of the medium of about 2 units (e.g. from 6.5 to 8.5) consistent with the higher soil pH of certain domains in microaerophilic soils. Other heterotrophic pathways involving the nitrogen cycle are the ammonification of amino acids and the denitrification (Hammes and Verstraete, 2002). Similarly to urea hydrolysis, the first process is mediated by both aerobic and anaerobic bacteria, whereas the second is strictly anaerobic.

The likely sources of urea and/or amino acids in prairie soils are animal waste or synthetic fertilizers. Although leases around many abandoned or suspended wells are cultivated by farmers, many wells, including the two Edam wells A3 and A4 and the Maidstone well A10, are located away from potential sources of animal waste and/or synthetic fertilizers. Another argument against the involvement of urea and amino acids in bacteriogenic calcite precipitation is the low $\delta^{13}C$ composition of calcite. Hydrolysis of urea involves several steps, including the formation and further hydrolysis of carbamate to ammonia and carbonic acid, which equilibrate in water to form bicarbonate, ammonium, and hydroxide ions (Hammes *et al.*, 2003). As a result calcite carbon is inherited from the urea and the two should therefore, have similar $\delta^{13}C$ compositions. Bacteriogenic calcite, however, has $\delta^{13}C$ composition as low as -57 ‰ indicating that bacterial oxidation of natural gas (methane) is the sole source of calcite carbon.

Calcite precipitation and methanogenesis

Methanogenesis is the second important bacterially mediated in microaerophilic soil near the leaking wells (Chapter 3). Bacterially mediated precipitation of calcite and dolomite is reported in methanogenic environments (Maliva *et al.*, 2000; Roberts *et al.*, 2004). Calcite of apparent authigenic origin is also identified in landfills by SEM imaging and carbon stable isotope analysis (Manning, 2001). Subsurface bacteriogenic processes involving fermentation of oil and coal are associated with the formation of carbonate (calcite) cements that have $\delta^{13}C$ between -32 and +24 ‰ (cf. Dimitrakopoulus and Muehlenbachs, 1987). Very high $\delta^{13}C$ values of carbonate cements associated with the tar sands of the Athabasca deposits (e.g., +24 ‰; Ringham, 1986) indicate that the former can only have formed as a result of methanogenesis via CO_2 reduction and the related extreme enrichment of residual CO_2 with ^{13}C. Therefore, bacteriogenic calcite precipitation in soil near the leaking wells could be related to methanogenesis. The $\delta^{13}C$ and $\delta^{18}O$ compositions of selected calcite and bulk soil samples at Edam, however, are consistent with precipitation in the spring, when soil temperatures are low, and methanogenic activity low (see Chapter 3). Therefore, calcite precipitation should be related to other microbial processes.

Authigenic calcite precipitation and other TEAP's

Anaerobic oxidation of hydrocarbons is mediated by strict anaerobes that use NO_3^-, Mn^{4+}, Fe^{3+} and SO_4^{2-} as electron acceptors instead of oxygen, and it is also capable of elevating the alkalinity and/or pH of the soil solution. (Castanier *et al.*, 1999). The choice of a particular electron acceptor depends upon availability, and in some instances, there is evidence that more than one acceptor is involved with the anaerobic oxidation of liquid hydrocarbons. Although several strains of bacteria capable of anaerobic oxidation of liquid hydrocarbons have been isolated from various environments, anaerobic oxidation of methane, is related to a specific consortium of microorganisms that uses SO_4^{2+} as an electron acceptor and has been found only in the soft sediments on the ocean floor (Hinrich *et al.*, 1999; Boetius *et al.*, 2000). In contrast to aerobic oxidation, the anaerobic oxidation of methane raises the carbonate alkalinity of the medium and also provides hydrogen sulphide to form pyrite. Authigenic carbonate precipitation in marine environment has long been associated with the anaerobic oxidation of methane from cold seeps at the sea floor (Rodriguez *et al.*, 2000; Aloisi *et al.*, 2002). The deposition of framboid pyrite in marine sediments is widely regarded as a biologically mediated process, in which organic carbon is used by sulphate reducing bacteria to produce H_2S. Framboid pyrite of apparent bacteriogenic origin is found in close proximity to bacteriogenic calcite in shallow samples near well A3 (Chapter 4). The low abundance and small sizes of bacteriogenic calcite and pyrite aggregates in the soil near well A3 indicate that these precipitated in small, isolated pools of soil solution. Even in seawater, bacteria manage to create and maintain microenvironments of distinct chemistry (Thompson, 2001). Therefore, the establishment and maintenance of conditions favorable of calcite precipitation in parts of the soil near the leaking wells should be facilitated by the isolated nature of those water pools. The discovery of pyrite closely associated with bacteriogenic calcite in the shallow soil near well A3 it is thus an argument in favor of the existence of isolated domains in the soil, where anaerobic oxidation of gaseous or liquid hydrocarbons facilitates calcite precipitation. The most significant limitation to the use of SO_4^{2-} for anaerobic oxidation in soils is availability, however (Chapter 3). In addition, as mentioned in Chapters 3 and 5, microbiological assays with soil samples collected at different depth near well A3 have not produced evidence of SO_4^{2-} related anaerobic oxidation so far (Boetius, 2005, personal communication).

Nitrate, and Fe^{3+} (Mn^{4+}) have also been suggested as electron acceptors used by bacteria to oxidize anaerobically methane and/or other gaseous and liquid hydrocarbons in terrestrial environments. Bacterial reduction of NO_3^-, or denitrification, has been associated with anaerobic oxidation of liquid hydrocarbons (Burland and Edwards, 1999) and more recently with the anaerobic oxidation of methane in sewage slurries (Islal-Lima *et al.*, 2004) according to the reaction:

$$5CH_4 + 8NO_3^- \leftrightarrow 5CO_2 + 4N_2 + 8OH^- + 6H_2O \quad [6\text{-}4]$$

The presence of nitrite and the elevated nitrite/nitrate ratios in deep soil near the Edam wells suggests that denitrification, or other processes related to the nitrogen cycle, may be associated with calcite precipitation (Chapter 3). Other studies, however, suggest that anaerobic oxidation of methane should be inhibited by the presence of even small amounts of nitrate (Segers, 1998). Laboratory incubation studies also demonstrate that Fe_3^+ stimulates anaerobic methane oxidation in rice paddies (Kumaraswami *et al.*, 2001). Subsurface sediments may contain up to several weight percent iron hydroxides which makes the Fe^{3+} a more abundant electron acceptor than NO_3^- Mn^{4+} and SO_4^{2-} (Ferris and Roden, 2000). In addition, the iron-reducing bacteria are known to keep hydrogen and acetate concentrations below the levels needed by sulphate reducing bacteria, thereby effectively out competing the latter (Ferris and Roden, 2000). The presence of siderite of likely authigenic origin in a crust sample from the casing of well A9 at Aberfeldy also provides evidence for Fe^{3+} reduction that could be related to the anaerobic bacterial oxidation of gaseous or liquid hydrocarbons.

Bacterially mediated calcite precipitation and preservation

Bacterially mediated precipitation of calcite is reported from environments where ambient pH is so low that the mineral should dissolve (Oelssner *et al.*, 2003). The presence of calcite in microaerophilic soil, therefore, suggests that bacteria play an important role, not only in precipitating, but also in preserving calcite in parts of the soil near the wells. SEM imaging of calcite from a pendant collected near well A10 provides evidence for the important role of bacteria in the preservation of calcite. Although bacteria and microbial film are not seen in this sample, calcite morphology is similar to this of bacteriogenic calcite at Edam, hence suggesting bacteriogenic origin (Chapter 4). A close examination of the sample reveals evidence of mild calcite dissolution (Chapter 4; Fig. 4-18b) suggesting that the pendant was not in place at the time of collection. Exposure to O_2 due to changing conditions in the upper soil at the site likely resulted in a demise of the bacterial community. As a result, calcite became unstable and began dissolving. Therefore, the preservation of bacteriogenic calcite, or other minerals of bacteriogenic origin, may be a rare phenomenon once the bacterial communities responsible for mineral precipitation and preservation die out.

Soil organic matter at the Edam research site

The $\delta^{13}C$ of soil organic matter in the microaerophilic soil around the wells is comparatively low. Although anaerobic bacteria, such as the methanogens and acetogenic bacteria, may also use CO_2 (HCO_3^-) produced by the oxidation of CH_4, the most important bacteriogenic process in microaerophilic soil is aerobic oxidation of CH_4, and hence SOM should be of predominantly methanotrophic origin. Depending on the type of microorganisms and on the growth conditions, methanotrophic bacteria produce organic matter that has $\delta^{13}C$ composition lower than that of methane being oxidized (Symmonds *et al.*, 1994; Jahnke *et al.*, 1999). Methanotrophic bacteria that use the ribulose monophosphate cycle for carbon assimilation produce biomass that could be as much as

30 ‰ lower than the $\delta^{13}C$ of methane. However, the $\delta^{13}C$ of SOM at the monitoring sites is significantly higher than that of CH_4 suggesting that the fraction of recent (labile) soil organic matter produced by the methanotrophic bacteria is low. The low fraction of SOM of methanothrophic origin appears consistent with its mineralization by a methanogenic consortium as discussed in Chapter 3. Preferential mineralization of labile SOM would lead to the preservation of recalcitrant SOM of high $\delta^{13}C$ and would explain the low content and relatively high $\delta^{13}C$ of SOM in microaerophilic soil. Soil samples used in this study were collected in 2001 and 2002. Therefore, it is possible that microaerophilic soil near the wells was, in fact, anaerobic prior to the disturbance caused by the installation of the soil gas probes. Anaerobic conditions would have prevented the accumulation of significant amounts of low $\delta^{13}C$ biomass of methanotrophic origin.

Conclusions

The $\delta^{13}C$ compositions of authigenic soil carbonates of abiotic and bacteriogenic origin collected near the leaking wells at Edam and Aberfeldy indicate the incorporation of a significant amount (i.e., up to 100 %) of methane-derived carbon. In contrast, carbonates collected in soil contaminated with heavy oil at Maidstone have $\delta^{13}C$ compositions consistent with the involvement of carbon produced predominantly from the bacterial oxidation of oil. The $\delta^{13}C$ of the authigenic soil carbonates at this site, however, is too high to be in isotope equilibrium with soil CO_2 collected during the monitoring period. It is thus, possible that methanogenesis contributed a larger fraction of carbon dioxide at this site in the past.

Precipitation of methane-derived carbonate at Edam and Maidstone is confined to microaerophilic soils. The lack of accumulation of methane-derived carbonate in the oxygen-rich soil near the two Edam wells indicates that authigenic carbonate precipitation is either very slow, or does not occur at all. Estimated rates of soil carbonate precipitation near the leaking wells are between 1 and 3 orders of magnitude higher than rates of pedogenic carbonate precipitation in arid soils. Authigenic calcite formation, however, is limited by the amount of Ca^{2+} available mostly in the form of pre-existing soil carbonate. There is no difference in the estimated rates of bacteriogenic and abiotic calcite precipitation.

Aerobic oxidation of natural gas and/or oil produces large amounts of CO_2 and it is, thus, not consistent with the precipitation and/or preservation of soil calcite. Therefore, bacteriogenic calcite formation should be associated with processes other than aerobic methane oxidation. Long term monitoring of a variety of environmental parameters (e.g., $\delta^{13}C$ of CO_2, $\delta^{18}O$ of soil moisture; soil temperature) indicates that bacterially mediated calcite precipitation at Edam likely occurs in a short time interval in the late spring. Low soil temperatures at that time of the year are inconsistent with significant methanogenic activity, which suggest that bacteriogenic calcite precipitation may be related to other TEA processes such as anaerobic oxidation of hydrocarbons or biomass. The presence of nitrite and the elevated nitrite/nitrate ratios in deep soil near the Edam wells suggests that denitrification, or other processes related to the nitrogen cycle, may be associated with calcite precipitation (Chapter 3). Trivalent iron is another alternative electron acceptor, due to its availability and ability for "regeneration".

Lack of abiotic carbonates and carbonate crusts in shallow soil at Edam and also in the upper 0.7 to 1.0 mbs of the well casings, suggests that ambient conditions are not favorable of carbonate precipitation. Small amounts of bacteriogenic calcite, however, are found in shallow soil at Edam. The finding of bacteriogenic calcite in microaerophilic soil underscores the role of bacteria in modifying the local environment, not only to precipitate calcite but also to preserve it.

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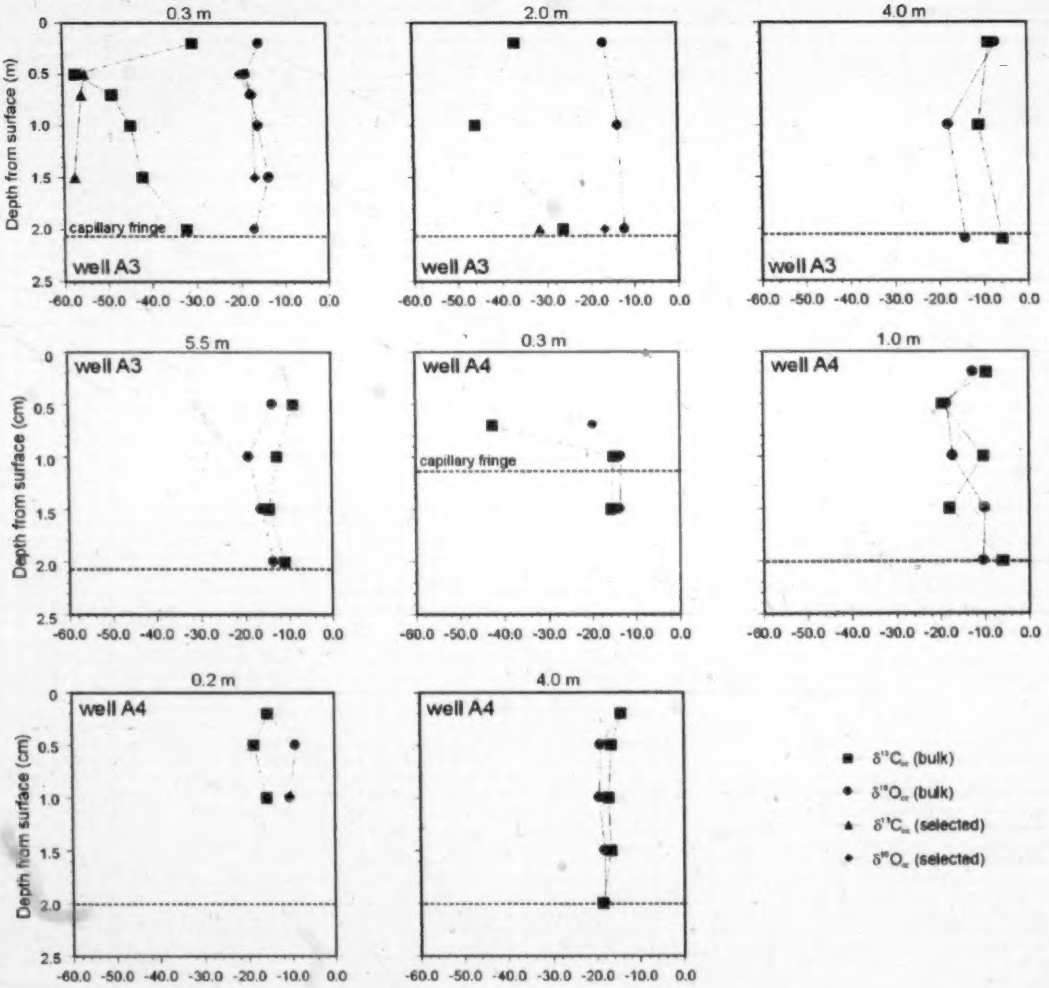


Figure 6-1 Carbon and oxygen stable isotope compositions (‰, VPDB) of bulk and selected soil carbonate samples collected in microaerophilic and oxygen-rich soil near wells A3 and A4, Edam. The lateral distance (m) of every soil profile from the respective well bore is denoted on the top of each grah.

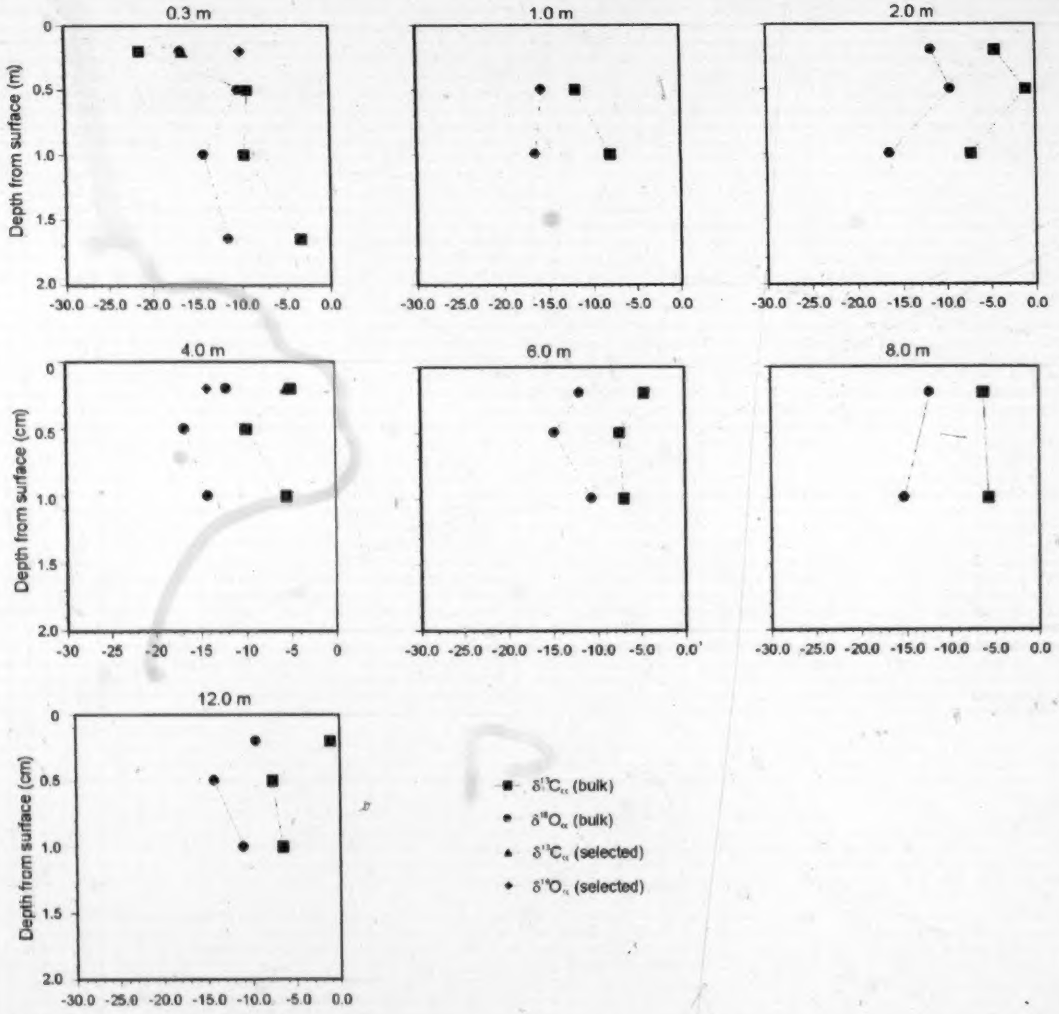
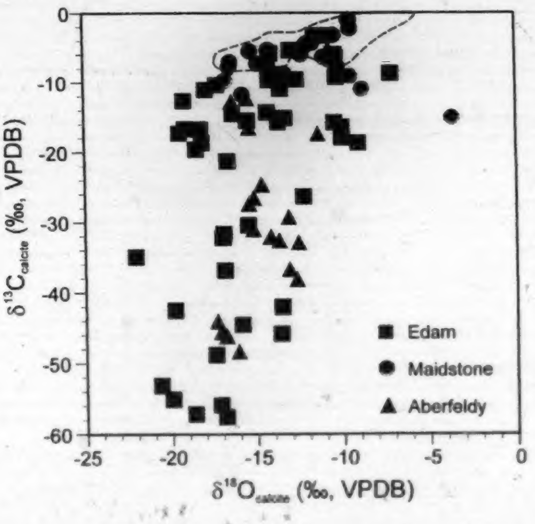


Figure 6-2 Carbon and oxygen stable isotope compositions (‰, VPDB) of bulk and selected soil carbonate samples collected in microaerophilic and oxygen-rich soil near well A10, Maidstone.



6-3 Oxygen and carbon stable isotope composition of soil carbonates collected from all sites at Edam, Maidstone, and Aberfeldy. The outlined area corresponds to measured isotope composition of soil carbonates in Western Canada (Chapter 5).

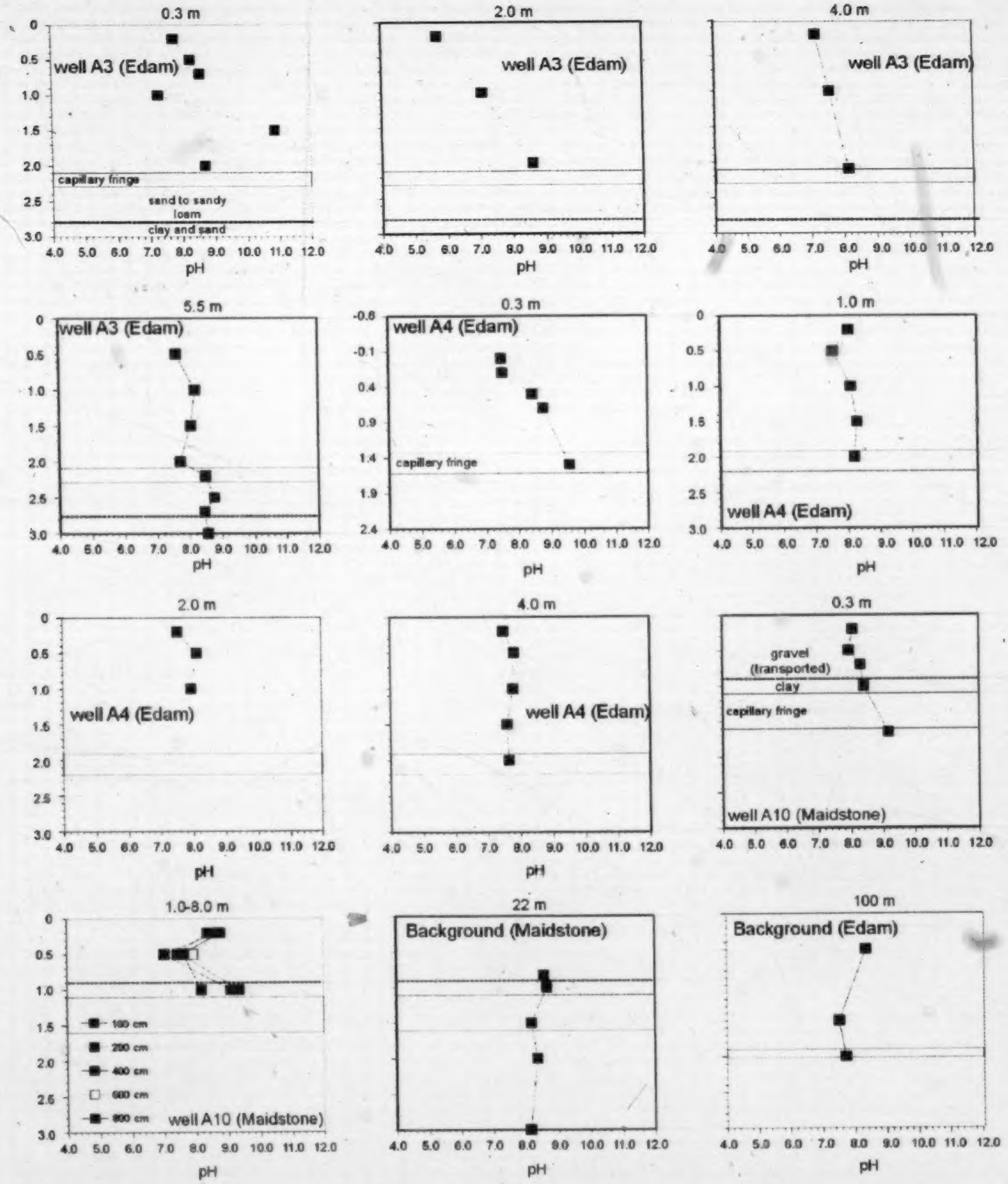


Figure 6-4 Soil pH of samples collected at different distances and depths from the well bores at the three research sites (i.e. A3, A4, and A10). Also included are the background locations. One at 22 m west from well A10 (Madstone), and the other at 100 m west from well A3 (Edam).

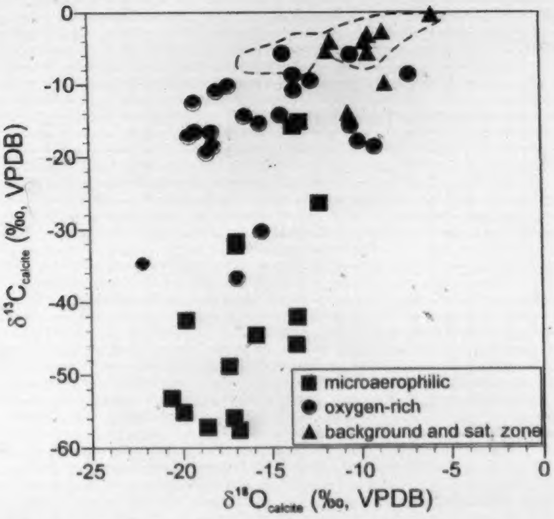


Figure 6-5 Oxygen and carbon stable isotope compositions of soil carbonates from the microaerophilic and oxygen-rich soils and of detrital and background soil carbonates at Edam.

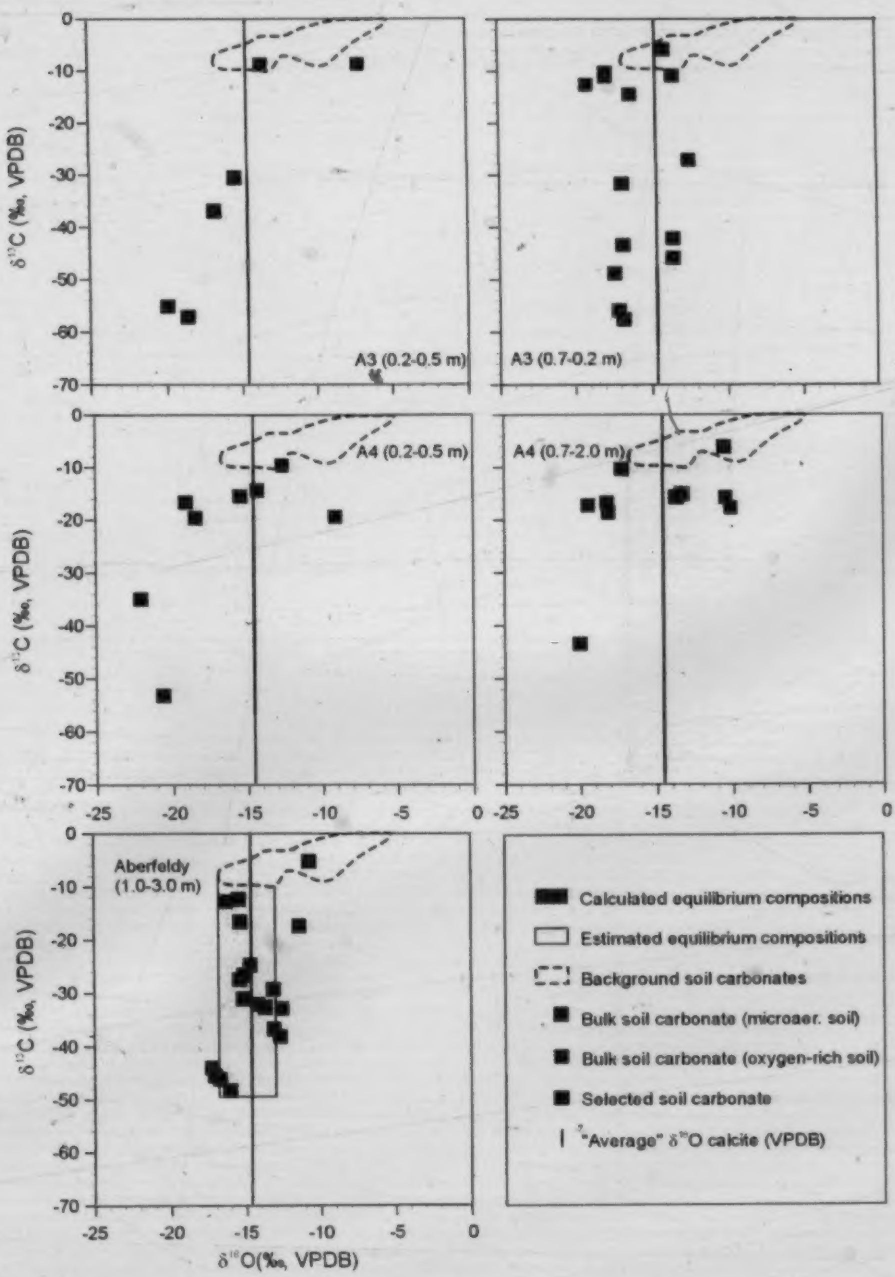


Figure 6-6 A comparison between calculated/estimated compositions of calcite that would precipitate in equilibrium with soil CO2 and soil moisture at Edam and Aberfeldy and measured $\delta^{13}C$ and $\delta^{18}O$ compositions (‰, VPDB) of soil carbonate samples collected at these sites.

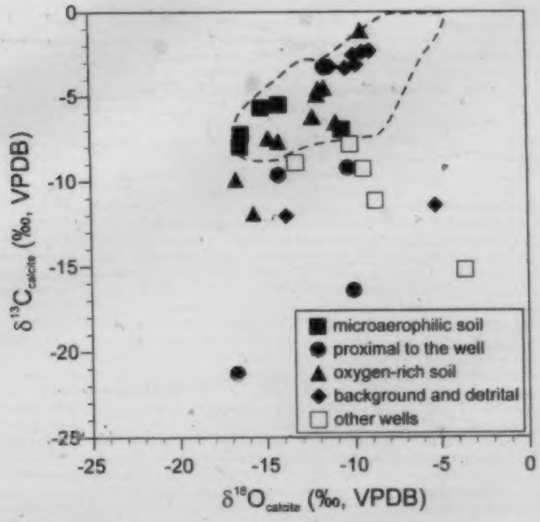


Figure 6-7 Oxygen and carbon stable isotope compositions of soil carbonates from the microaerophilic and oxygen-rich soils and also from detrital and background soil carbonates at well A10 at Maidstone. The compositions of samples from the rest of the wells at Maidstone are also plotted on the diagram.

Ch[illegible]

Summary and implications

Summary

This study demonstrates that several bacterially mediated processes occur in soil near wells that leak natural gas in Western Canada. These include aerobic oxidation of methane and/or liquid hydrocarbons, methanogenesis, and bacterially mediated precipitation of calcite. Anaerobic oxidation of gaseous and/or liquid hydrocarbons is also suspected but is yet to be proven. The study also examines the relationship between soil respiration and authigenic carbonate precipitation in soil away from the leaking well sites. A brief summary of the results is presented below.

Aerobic bacterial oxidation of gaseous and/or liquid hydrocarbons is the most significant bacterially mediated process in soils near the wells. Natural gas consumption at two well sites near Edam, Saskatchewan, where soil is not contaminated with liquid hydrocarbons, approaches 100 % in the summer. The fraction of methane oxidized in microaerophilic soil at one metre below the soil surface and in close proximity to the well bores change little in the winter indicating that methanotrophic bacteria are well adapted to survive near freezing temperatures. By eliminating methanotrophy in the upper one metre of the soil column, however, soil freezing reduces overall methane consumption at the two sites by 40-60 %.

Estimated kinetic isotope effects related to the oxidation of methane to carbon dioxide, at the two Edam wells, exhibit significant seasonal variability and correlate negatively with soil temperature. The slopes of the correlation lines have higher values than those determined from previous studies, and for samples collected at Edam vary from 0.9 to 1.3. Results from this study suggest that the negative correlation between isotope fractionation and temperature results from temperature related variation of the activity of the methane monooxygenaze enzyme (MMO), and not from decreasing cellular densities, as suggested previously by Templeton *et al.* (2006). High natural gas concentrations away from the well bores and comparatively high $\delta^{13}C$ of soil CO_2 (i.e., ca. -30 ‰) collected from one research site near Maidstone, Saskatchewan that is contaminated with liquid hydrocarbons indicate significant reduction of the ability of methanotrophic bacteria to oxidize leaking natural gas at those sites. The reduction is likely driven by the presence of higher energy substrates (i.e., heavy oil and/or byproducts of its oxidation), and/or by a competition between the methanotrophic bacteria and the oxygen consuming microorganisms that metabolize these substrates. These findings are consistent with the results of the review of a large data base of soil gas samples collected at the University of Alberta that shows little evidence of natural gas oxidation at a large number of leaking well sites. Therefore, both the harsh climate in Western Canada and oil contamination play very important roles in inhibiting bacterial oxidation of leaking natural gas.

Elevated H_2 gas concentrations, soil pH, and a significant discrepancy between the KIE values determined by using the $\delta^{13}C$ of residual CH_4 and produced CO_2, and the $\delta^{13}C$ of initial CH_4 and residual CH_4, respectively, reveal that bacterial methanogenesis also occurs in microaerophilic soil at the two Edam well sites. The coexistence of methanogenic and methanotrophic bacteria is one of the most important findings of this study. Although methanogenesis is common in soils contaminated with liquid hydrocarbons, this is the first time it has been detected in soils contaminated by natural gas only. By consuming nearly all available oxygen, methanotrophic bacteria render parts of the soil near the wells anaerobic, thereby providing a habitat to a consortium of fermenting, acetoclastic, and methanogenic microorganisms. The conspicuous lack of biomass of methanotrophic origin in the soil at Edam, evident from the low concentrations of SOM and the comparatively high $\delta^{13}C_{SOM}$, suggests that fermenting bacteria metabolize lysed cells and polysaccharide film left from the methanotrophic bacteria. However, the estimated amount of bacteriogenic methane that is generated by the methanogens is small (e.g., 5-10 % v/v) and not likely to have a significant environmental impact.

The discovery of authigenic pyrite and the complete absence, or very low concentrations, of SO_4^{2+}, NO_3^- and NO_2^- in the microaerophilic/anaerobic soils at the two leaking well sites near Edam provide geochemical evidence that anaerobic oxidation of natural gas occur(ed) there. The framboid texture of pyrite, found in close association with bacteriogenic calcite, is consistent with biological origin and suggests that pyrite formation may have been mediated by sulphate reducing bacteria. *In vitro* assays with anaerobic soil samples collected near one of the Edam wells, however, failed to demonstrate methane-based sulphide production (Boetius, A. 2005. Max Plank Institute for Marine Microbiology, personal communication). Thus, the limited supply of SO_4^{2+} in the unsaturated soil appears to have prevented the establishment of a sulphate based anaerobic bacterial community capable of metabolizing gaseous hydrocarbons. Although nitrate concentrations are low or below detection, comparatively high nitrite concentrations measured in a soil samples at one of the leaking wells at Edam suggest that a process related to the cycle of nitrogen could provide alternative electron acceptors for anaerobic oxidation of hydrocarbons. Due to its availability in shallow sediments and its ability for regeneration, trivalent iron may also be an alternative electron acceptor. The lack of analytical data, however, precludes speculations as of the role of Fe^{3+} in anaerobic microbially mediated processes near the leaking wells.

Optical, SEM, EDS and XRD investigations of soil samples established the presence of several authigenic (anthropogenic) minerals in soil samples collected near the leaking wells. These include calcite (normal and Mg-calcite), pyrite and siderite. SEM imaging also established the presence of two types of authigenic calcite: abiotic and bacteriogenic. Abiotic calcite is common in soils near the wells at Edam, as well as in scales that precipitate on the surfaces of well casings at Aberfeldy, Saskatchewan. Bacteriogenic calcite, however, is found only in microaerophilic soil in the zones of hydrocarbon oxidation at Edam. SEM imaging shows mineral growth on microbial surfaces and evidence of replacement indicative of the active role of microorganisms in calcite precipitation.

Most carbonate samples collected near the leaking wells at Edam and Aberfeldy have low $\delta^{13}C$ compositions indicative of the incorporation of methane-derived carbon. Rates of soil carbonate precipitation in the microaerophilic soil near the Edam wells are between 10 and 30 times higher than the rates of authigenic carbonate precipitation in arid soils. Accumulation of significant amounts of authigenic calcite near the wells, however, is limited by the lack of Ca^{2+}, available mostly in the form of pre-existing soil calcite.

The low soil pH and low amounts of carbonate in oxygen-rich soil near the wells indicates that the high quantities of CO_2 produced from the aerobic oxidation of hydrocarbons prevent authigenic carbonate precipitation in the shallower soils around the leaking wells. The association of pyrite with bacteriogenic calcite indicates that at least in some instances the precipitation of bacteriogenic calcite occurred in an anoxic environment. The most likely processes associated with the precipitation of bacteriogenic calcite are methanogenesis and anaerobic oxidation of liquid and/or gaseous hydrocarbons. The low $\delta^{13}C$ of the bacteriogenic calcite, however, suggests that the last process is most likely responsible for the precipitation of authigenic calcite precipitation in the microaerophilic soils at Edam. This is corroborated by SEM imaging and the long-term monitoring of several local environmental parameters (e.g., $\delta^{13}C$ of soil CO_2; $\delta^{18}O$ of soil moisture; soil temperature), suggesting that bacterially mediated calcite either formed out of isotope equilibrium, or precipitation occurred in spring when soil temperatures are too low for methanogenesis.

The $\delta^{13}C$ composition of samples containing the highest percentage of authigenic calcite at Maidstone is too high to be in isotope equilibrium with $\delta^{13}C$ of CO_2 measured during the monitoring period. Therefore, the precipitation of authigenic carbonates at this site in the past was most likely associated with methanogenesis related to the mineralization of spilled heavy oil at the site.

Estimated soil respiration rates in sandy uncontaminated soil near the two monitoring sites at Edam exhibit strong seasonal variability and are on the lower end for those determined for arid areas. Measured $\delta^{13}C$ compositions of soil organic matter at Edam are low (i.e., between -25 and -30 ‰) and are indicative of C_3 plant origin. Partial overlap of the stable isotope compositions of background carbonates from the saturated zone at Edam with those of published soil carbonates collected in central Saskatchewan casts doubt on previous estimates of the amounts of authigenic carbonate precipitation in Western Canada (cf. Landi, 2000). The results from a one-dimensional diffusion model of Cerling (1984) and the oxygen stable isotope compositions of soil carbonate samples indicate that authigenic carbonates at Edam and Maidstone precipitated in the summer as the result of water loss related to evaporation.

Implications for the oil industry and regulatory agencies in Western Canada

Methane is the second important greenhouse gas, and thus every effort should be made to prevent or minimize undesired releases to the atmosphere. The near complete oxidation of natural gas at the Edam well sites in the summer is consistent with results of previous studies, which demonstrate that sandy soils at comparatively low water saturation provide favourable environment for aerobic methanotrophic bacteria. Review of the carbon stable isotope compositions of hydrocarbon gases and carbon dioxide in gas samples from the University of Alberta database, however, reveals little or no evidence of methane oxidation at a significant number of leaking well sites. Results demonstrate that soil freezing and the presence of liquid hydrocarbon contamination are the two most important inhibitors of aerobic bacterial oxidation of natural gas in soil. Results also imply that high leaking gas rates, low soil permeability or shallow groundwater levels could also decrease or prevent the oxidation of leaking gas, hence rendering this process largely ineffective in reducing natural gas emissions at a large number of well sites.

Although leaking natural gas in most parts of Western Canada does not contain H_2S, and leaking gas is considered non-toxic, reports of stunted vegetation near the leaking wells (cf. Rowe and Muehlenbachs, 1999) and the anecdotal cases of exploded residential water wells and gas discharges from kitchen faucets (Nikiforuk, 2006), have had a significant negative impact on the public opinion in both Alberta and Saskatchewan. The recent unprecedented surge of drilling for coal bed methane (CBM) in the Province has also generated a significant concern in the rural community in Alberta due to the possibility for natural gas contamination of the shallow potable water aquifers (Klaszuk, 2006).

Therefore, the Provincial governments and the oil and gas industry should maximize every effort, not only to prevent natural gas leakage, but also remediate all existing leakages of natural gas.

Carbon stable isotope fingerprinting is one of the best methods for leaking gas source identification (Rowe and Muehlenbachs, 1999). This study demonstrates, however, that bacterial oxidation of leaking gas alters significantly the $\delta^{13}C$ of the individual hydrocarbon gases (Chapter 3), thus rendering proper identification of the sources of gas leakage impossible. The results of this study also demonstrate that leaking soil and surface casing vent gases at a number of oil and gas well sites originate in different geological units. Thus, to effectively eliminate gas leakages, samples of both the SC vent and soil gases should be acquired. Another requirement for a successful identification of the leaking gas source of soil gases is that these should not be impacted by bacterial oxidation. To obtain soil gas samples that have the least altered isotope compositions, permanent soil gas probe(s), similar to those used in this study, must be installed proximal to the source of gas leakage, which, as demonstrated in Chapter 3, is located at the intersection between the leaking well bore and the water table.

This study provides a strong impetus for the regulatory agencies in Alberta and Saskatchewan to review their policies regarding the remediation of leaking wells. Considering the success the use of $\delta^{13}C$ analyses had in identifying the sources of leaking gases, the agencies should establish strict guidelines for the collection, and interpretation of the stable isotope compositions of soil gas samples by the oil industry and various service companies in Western Canada. Those guidelines will improve significantly the quality of the data provided by the analytical facilities in the Province, and will increase the rates of successful remediation of leaking wells, which will help in preventing the unwanted emissions of methane to the atmosphere in Western Canada.

Future work

1. Both laboratory incubation experiments with soil from the Edam sites and DNA fingerprinting by using polymerase chain reaction (PCR) are needed to provide further evidence of the presence of methanogenic bacteria in the microaerophilic soils near the leaking wells.

2. Lack of data on the rates of methane oxidation per volume of soil precludes estimates of the volume of sandy soil needed to optimize methane oxidation at the leaking well sites. Leaking gas rates should, therefore, be measured at the monitoring sites by excavating the well casings and installing gas capturing devices below the top of the saturated zone. The distribution of soil gases in the subsurface near the wells should be approximated by using a two-dimensional numerical model that includes both advection and diffusion.

3. Currently SEM evidence of bacteriogenic calcite precipitation is limited to few samples collected in shallow soil near one of the wells at Edam. More SEM work is, thus, needed to provide a better understanding on the spatial distribution of bacteriogenic calcite in the subsurface around the leaking wells.

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Appendices

Appendix 1. SCV gas from the University of Alberta database - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Date	UWI						C_1	C_2	C_3	C_4	C_5	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$^{13}C_{C4}$	$^{13}C_{nC4}$	$^{13}C_{CO2}$
		1	19	21	19	W3M	405941	665.8	61.5	23.0	4.9						-70.9	-58.9	-45.3	-31.6		
15.09.2003		1	33	21	20	W3M	175567	294.7	18.4	9.8	2.6						-72.7	-60.0	-44.1			
11.02.2004		1	33	21	20	W3M	362323	708.3	59.5	19.9	4.9	2.6					-68.5	-58.6	-45.7	-32.1		
05.11.2002	a	2	33	31	24	W3M	94109	4840.0	1124.0	104.9	81.5	40.4					-65.3	-40.1	-31.5	-31.9	-26.6	
		10	36	32	24	W3M	192757	414.0	134.0	60.0	162.0						-68.9	-31.6	-29.3	-29.4	-28.9	-24.5
22.08.2003	A	10	33	42	26	W3M	48757	115.1	13.2	2.7	1.1	10.0					-67.8	-42.9	-36.4	-30.6		
	a5	5	10	45	28	W3M	90277	9925.4	2646.7	1224.9	387.6						-62.3	-33.3	-28.5	-28.3	-29.4	
19.08.2002	a	10	23	46	28	W3M	122394	1116.7	319.1	95.5	51.7	23.1					-58.5	-40.4	-33.3		-29.8	-54.1
	a15	15	30	47	21	W3M	165879	325.5	36.3	13.4	3.2						-67.1	-45.5	-37.2	-29.7	-35.4	-11.2
		13	20	47	26	W3M	351267	1598.0	224.4	37.3	16.7						-62.7	-38.8	-31.8	-29.2	-29.0	-8.0
15.07.2003		13	27	48	18	W3M	34828	74.5	6.2	1.7	0.6	3.8		84.7	235.5		-70.5	-49:2	-36.7			-20.2
19.12.2003	b6	6	16	48	18	W3M	49206	82.4	8.2	2.4	0.7	1.0		112.5	1962		-72.1	-49.7	-41.0	-32.4		
27.09.2002		12	2	48	18	W3M	274979	512.0	45.6	15.3	3.9	0.0		763	5.0		-72.1	-50.4	-39.4	-30.4	-30.1	-20.0
22.09.2000	a11	11	5	48	18	W3M	434185	792.8	84.9	22.4	5.8	1.0					-69.2	-49.4	-40.0	-33.0	-36.3	-6.2
		4	19	48	19	W3M	149217	247.1	11.5	3.4	0.6	1.2					-53.1	-34.1	-33.3	-30.3		-57.1
20.08.2003		10	21	48	19	W3M	14347	42.5	3.2	2.5	0.9						-67.7	-39.6	-27.4	-30.6	-27.7	
		4	17	48	19	W3M	25733	20.6	2.5	0.8	0.4						-66.4	-42.8	-37.1	-28.8	-32.4	-16.1
13.01.2003		11	20	48	19	W3M	31318	53.2	7.5	2.7	0.5	0.8										-40.8
12.05.2004		1	18	48	19	W3M	79707	104.7	11.7	9.7	0.7	3.1					-66.8	-43.9	-38.1	-38.4	-29.0	
15.07.2003	2a	2	22	48	19	W3M	102917	188.3	17.0	5.6	1.4	4.3		112.8	302.7		-66.2	-46.8	-39.4	nm	nm	-25.8
24.09.2002		3	4	48	19	W3M	112100	400.0						100.0	200.0		-75.3	-46.8	-38.3	-26.8	-26.5	-11.2
30.09.2002	A11	11	15	48	19	W3M	116800	200.0				500.0		100.0			-67.3	-43.2	-37.6	-32.7	-35.4	-10.4
31.07.2003	a7	7	22	48	19	W3M	119168	241.1	22.1	4.6	3.0	1.0		111.3	9.1		-65.9	-42.1	-34.4	-28.5	-20.7	-40.0
		4	16	48	19	W3M	212703	470.3	36.5	6.4	3.4						-66.5	-42.2	-35.8	-29.5	-36.4	-57.8
20.08.2003	a2	2	32	48	19	W3M	221736	422.9	35.6	12.7	2.9	0.2					-70.9	-42.8	-40.6	-33.1	-30.2	-73.3
01.10.2002	d11a	11	15	48	19	W3M	306300	900.0						200			-64.9	-43.2	-37.6	-32.7	-35.4	-10.4
23.07.2003		1	18	48	19	W3M	339639	653.8	64.2	19.6	5.6	27.1		331.1	3.9		-66.6	-45.4	-38.8	-31.2	-23.5	-45.2
17.07.2003	a11	11	20	48	19	W3M	401194	752.8	66.6	21.2	5.1	12.9		455	7.4		-70.8	-45.7	-42.1	-34.3	-37.4	-45.7
7.10.2002	d3	3	8	48	19	W3M	423328	890.0	82.5	25.8	6.6			636.1	32.8		-71.4	-44.9	-40.2	-33.1	-30.9	-20.9
01.10.2002	c14	14	15	48	19	W3M	474800	1100.0						400	600.0		-64.7	-41.5	-36.7	-32.6	-36.5	-48.1
24.09.2002	a12	12	15	48	19	W3M	527500							600			-67.7					-61.6
18.05.2000		7	22	48	19	W3M	545145	1136.2	99.8	36.7	10.6						-65.4	-42.1	-34.6	-29.6	-34.3	-16.6
20.08.2003	a13	13	17	48	20	W3M	115200	248.9	37.2	30.6	35.2			248	0.0		-70.1	-45.6	-30.9	-28.0	-27.5	-52.4
20.08.2003	a15	15	19	48	20	W3M	205140	413.2	34.2	12.6	2.6						-68.8	-48.8	-40.5	-32.4		
30.07.2003	a15	15	9	48	20	W3M	205140	413.2	34.2	12.6	2.6			702	0.0		-68.8	-48.8	-40.5	-32.4		-64.2
05.08.2003	a13	13	17	48	20	W3M	209795	367.9	31.7	10.0	2.1	0.3					-70.2	-46.7	-41.0	-31.7	-35.9	-33.1
20.08.2003	4bL	12	9	48	20	W3M	336200	828.8	81.4	22.6	7.5			1371	0.7		-69.3	-51.0	-39.4	-32.6	-34.8	-70.2
	d11	11	19	48	20	W3M	446971	829.8	80.2	49.4	5.6	0.0					-70.0	-49.0	-41.0	-32.6	-36.8	-19.6
	d11	11	19	48	20	W3M	446971	829.8	80.2	49.4	5.6						-70.0	-49.0	-41.0	-32.6	-36.8	-19.6
	a9a	9	10	48	23	W3M	871	14.5	22.1	10.7	11.5						-60.1	-30.9	-28.6	-26.5	28.0	35.8
	a4	4	12	48	23	W3M	1258	23.6	28.9	10.5	13.0						-61.0	-34.1	-29.6	-28.1		-22.1
	d5	5	12	48	23	W3M	13245	48.6	10.1	3.2	3.7						-54.1	-42.2	-35.2	-31.3	-32.2	-14.6
	c3	3	12	48	23	W3M	45119	30.0	33.2	14.4	15.9						-50.7	-32.5	-28.5	-29.1	-29.2	-51.3
	2d8	8	11	48	23	W3M	230117	745.5	101.4	41.1	17.5						-64.2	-40.7	-34.8	-30.4	-29.8	-12.3
	d8	8	11	48	23	W3M	230117	745.5	101.4	41.1	17.5						-64.2	-40.7	-34.8	-30.4	-29.8	-12.3
	ddk	1	11	48	23	W3M	285164	486.4	47.9	21.3	5.6						-66.7	-43.3	-37.8	-30.3	-32.2	-43.3
	2B1	14	11	48	23	W3M	479656	1501.1	161.8	58.3	13.7						-66.0	-41.4	-34.5			
	b12	12	12	48	23	W3M	484672	1476.8	163.4	63.3	13.5						-65.0	-43.3	-39.7	-33.6	-35.1	-12.1
	1d9	9	11	48	23	W3M	498199	1476.2	152.5	57.0	13.7						-65.0	-42.4	-37.7	-33.4	-38.7	-4.4
		13	21	48	26	W3M	49893	136.1	12.3	3.2	1.3						-60.1	-40.6	-35.2	-27.5	-24.4	-15.8
	B1A	1	25	48	28	W3M	83	3767.0	368.0	56.0							-56.8	-38.4	-33.6	-32.6	-33.7	-18.7
		16	27	49	22	W3M	11392	26.0	1.6	0.7	0.8	3.9		1.6			-58.6	-40.4				-42.1
08.08.2002		3	27	49	22	W3M	16943	67.6	4.7	1.3	0.3	4.5					-54.3	-36.3	-41.0			-38.5
		10	27	49	22	W3M	17040	61.3	3.9	1.0	0.3						-67.1	-40.7	-37.5			
18.07.2002		9	27	49	22	W3M	152246	572.6	47.3	14.2	3.5						-53.9	-37.7	-37.7	-29.6	-28.1	-63.4
18.07.2002		1	27	49	22	W3M	158520	425.6	29.6	8.7	2.1						-66.2	-42.3	-40.0	-31.6	-30.7	-53.0
	a	1	35	49	22	W3M	159313	395.8	32.5	9.0	2.3						-72.4	-45.1	-37.9	-27.1		-16.8
	a12	12	16	49	22	W3M	161830	520.1	48.5	14.1	3.1						-55.1	-39.2	-35.3	-30.6	-35.0	
	a12	12	27	49	22	W3M	163859	421.0	30.4	13.8	1.7						-64.9	-42.1	-39.7	-35.4	-31.6	-28.0
27.06.2003		15	22	49	22	W3M	175567	397.9	28.1	7.6	1.9	0.6		0.0	This gas may		-73.8	-43.7	-40.3	-32.5		-14.7
19.11.2003		6	27	49	22	W3M	206912	439.3	33.9	9.2	3.2						-70.8	-43.2	-40.5	-33.4	-36.6	
		2	27	49	22	W3M	229838	548.9	39.6	10.2	2.6						-72.6	-45.7	-41.8	-35.4		
	a	6	27	49	22	W3M	241654	641.7	41.6	10.7	2.9						-68.1	-45.3	-42.6	-31.0	-27.5	-16.9
	a	2	27	49	22	W3M	270147	654.3	44.7	9.7	2.5						-70.0	-44.0	-40.6	-31.9	-33.1	-14.4
26.04.2002	a	2	2	50	25	W3M	16983	34.8	3.5	0.7	0.3	4.8					-66.3	-50.7	-42.3			-13.2
		1	21	51	23	W3M	165692	232.1	26.1	8.5	2.0	1.2					-67.2	-52.9	-40.6	-30.3		
		10	7	14	16	W4M	386422	772.6	40.1	4.7	1.1						-67.4	-41.1	-30.0	-27.7	-24.2	-31.9
		6	13	38	1	W4M	99738	1317.3	854.0	311.1	203.0						-62.3	-34.1	-29.1	-28.8	-28.9	-19.1
23.09.2003	d	6	30	45	6	W4M	3161	180.2	38.4	231.4	640.9	1419.0					-62.7	-29.0	-26.7	-24.5		
	10d	10	4	50	6	W4M	507599	755.3	58.1	58.8	6.3						-65.2	-46.4	-39.3	-33.7	-34.9	-18.8
	7A	7	7	52	3	W4M	211200	300.0	0.0	0.0	0.0	0.0					-69.4	-46.4	-39.8	-34.3		
	7a	7	7	52	3	W4M	237687	84.2	8.5	9.0	0.6						-63.8	-40.6	-36.2	-29.3		-57.1
	a1	1	9	52	4	W4M	468026	1178.9	129.7	27.1	10.9						-62.3	-48.7	-41.1	-32.8	-34.7	-22.6
22.08.2002	D	10	22	52	7	W4M	317473	66.4	7.3	9.8	1.1						-58.9	-34.1	-36.0	-30.1	-32.0	
	b	5	33	55	3	W4M	10599	108.6	4.8	1.0	0.6	16.3		16.2	66.5		-57.3	-27.9	-29.3	-26.8	-22.6	-28.0
	c	5	27	55	3	W4M	134146	142.9	8.1	2.4	3.0						-55.0	-26.7	-29.6			-18.9
	14a	14	23	55	6	W4M	208038	452.1	40.3	19.0	3.1						-67.1	-51.3	-41.5	-33.3	-35.9	-10.7
	a14	14	23	55	6	W4M	472355	1031.3	90.7	48.1	8.2						-63.5	-50.7	-41.9	-33.2	-36.9	-13.1
	A	1	8	56	4	W4M	101810	192.0	13.8	3.0	1.2	6.6					-65.9	-50.2	-43.0	-33.3		-21.8
	d	5	15	57	5	W4M	209171	638.5	53.7	9.8	3.5						-60.0	-38.3	-32.0	-27.4	-28.2	-12.3
12.10.2004	a	12	29	61	3	W4M	35634	123.0	2.1	1.0	0.5						-73.7	-49.1	-26.2			-10.5
		15	23	68	21	W4M	202837	471.8	35.4	21.1	4.9						-63.6	-45.1	-39.0	-31.5	-32.5	-27.3
							320916	978.8	125.7	51.4	18.0						-64.7	-41.8	-39.1			-3.2

Appendix 1. SCV gas from the University of Alberta database - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

(cont.)

Date	UWI						C_1	C_2	C_3	C_4	C_5	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$^{13}C_{iC4}$	$^{13}C_{nC4}$	$^{13}C_{CO2}$
		1	19	21	19	W3M	879163	1823.0	164.3	55.9	12.7	3.8					-69.4	-58.2	-44.3	-31.4	-37.2	-13.8
		14	28	31	23	W3M	891911	6085.9	2148.6	2135.8	706.9						-56.6	-34.8	-28.0	-31.0	-29.0	-9.7
	7c	12	36	45	23	W3M	962337	2449.7	215.2	40.9	19.9						-66.8	-47.8	-38.1	-33.5	-38.2	
	5c	7	3	46	23	W3M	941141	2619.6	255.5	49.1	22.3						-63.6	-49.3	-39.7	-32.7	-37.7	
		15	30	47	21	W3M	927619	2365.1	245.2	42.4	22.3						-64.2	-45.3	-36.4	-30.1	-30.2	-15.3
	a1	1	6	47	23	W3M	907595	2515.4	277.0	91.1	24.0						-66.2	-43.6	-36.1	-30.6	-28.9	
		11	20	47	26	W3M	975325	5467.7	799.6	123.7	57.5						-61.7	-38.4	-31.2	-28.8	-28.6	
27.09.2002	a11	11	5	48	18	W3M	666280	1482.0	132.9	36.6	9.3	18.0		1622	82.3		-70.5	-49.3	-39.6	-31.7	-36.7	-28.2
19.12.2003	a11	11	5	48	18	W3M	785866	1351.0	156.2	48.6	13.0	1.0		1748	14.9		-70.0	-49.3	-40.2	-32.6	-37.3	
26.04.2002	a11	11	5	48	18	W3M	815500	1579.0	162.8	42.3	10.5	0.0		6468	5.7		-73.1	-49.1	-40.0	-31.1	-34.1	-18.4
25.04.2002		12	2	48	18	W3M	823136	1897.0	191.9	44.9	13.3	5.4		5808	1.7		-70.4	-48.9	-39.3	-31.3	-34.4	-24.5
22.09.2000		12	2	48	18	W3M	879528	1891.0	197.1	108.6	15.2	0.0					-72.1	-50.4	-39.4	-30.4	-30.1	-20.0
22.09.2003		12	2	48	18	W3M	879528	1891.0	197.1	108.6	15.2	1.0					-72.5	-50.3	-40.2	-32.8	-36.3	
15.12.2004	a11	11	16	48	19	W3M	560500	2200.0	200.0								-68.2	-34.0				-39.8
15.07.2003	8a	8	22	48	19	W3M	616201	1222.0	109.2	19.7	11.4	16.8		920	492.2		-65.7	-42.8	-32.6	-26.5	nm	-60.0
18.12.2003	a13	13	19	48	19	W3M	628748	1381.0	129.4	33.9	12.2	4.8		700	38.0		-69.1	-43.0	-38.0	-30.5	-30.2	
12.08.2000	a11	11	20	48	19	W3M	672219	1206.4	129.2	87.3	10.1	35.8					-69.0	-44.8	-39.9	-34.4		
01.10.2002	b5	5	29	48	19	W3M	738300	1500.0						600			-69.4	-44.2	-40.2	-31.6	-33.6	-28.5
01.10.2002	a16	16	10	48	19	W3M	740700	1300.0						800	300.0		-68.4	-48.5	-41.0	-33.0	-40.1	-7.7
24.09.2002	4	4	22	48	19	W3M	784900	1500.0						1000			-65.8	-41.4	-35.2	-31.7	-31.4	-18.6
24.09.2002	a4	4	22	48	19	W3M	784900	1500.0						1000			-63.8	-41.4	-35.2	-31.7	-26.3	-18.6
20.09.2002	a14	14	8	48	19	W3M	787500	1500.0	100.0					700	400.0		-68.3	-45.5	-37.6	-30.1	-34.4	-21.3
30.09.2002	c9	9	10	48	19	W3M	793700	1200.0						1600	200.0		-68.3	-44.6	-37.2	-30.6	-32.4	-11.2
01.10.2002	c6	6	16	48	19	W3M	882200	1800.0						700	100.0		-66.0	-39.3	-34.1	-32.0	-33.1	-19.8
28.10.2002	a6	6	16	48	19	W3M	882200	1800.0						700	100.0		-66.0	-39.3	-34.1	-32.0	-33.1	-19.8
30.05.2001	a14	14	8	48	19	W3M	887109	1748.2	150.3	52.4	14.8						-69.1	-45.9	-40.3	-31.8	-37.5	-23.9
		1	18	48	19	W3M	889308	1598.5	178.6	47.3	14.7						-69.5	-46.1	-38.8	-38.4		
05.05.2004	c	2	1	48	22	W3M	868514	2057.0	231.6	58.6	23.1	1.0					-68.3	-45.0	-37.0	-29.7	-35.6	
	b3	3	12	48	23	W3M	552462	1755.9	225.3	93.1	28.8						-63.8	-41.7	-36.6	-32.4	-31.6	-13.9
	c5	5	12	48	23	W3M	573202	1848.3	203.4	79.5	19.2						-62.0	-40.8	-35.4	-31.2	-34.4	-10.6
	2B1	14	11	48	23	W3M	615791	1993.4	213.4	29.3	14.7						-65.0	-41.6	-34.3	-29.6	-28.8	-14.1
		5	14	48	23	W3M	695463	2818.4	285.3	58.5	26.1	27.2					-66.7	-39.0	-34.2	-30.3	-28.3	
	d10	10	11	48	23	W3M	702785	2371.7	268.1	112.0	25.6						-64.2	-41.8	-37.6	-33.1	-32.9	
	B4	4	12	48	23	W3M	780700	2700.0	400.0	0.0	0.0	0.0					-64.2	-41.7	-37.3	-32.8	-38.1	
	c16	16	11	48	23	W3M	846368	2576.1	275.6	99.3	24.6						-64.9	-41.1	-34.8	-29.4	-31.5	-10.8
	4c1	12	11	48	23	W3M	872235	3071.7	380.8	163.7	35.1						-64.6	-40.9	-34.6	-30.8	-34.5	
	c	5	14	48	23	W3M	882403	3101.1	359.1	70.7	34.7	23.1					-64.2	-40.4	-34.2	-29.2	-31.9	
	2D8	8	11	48	23	W3M	888590	3026.1	336.9	135.0	29.3						-64.9	-40.9	-37.0	-34.3	-39.9	
	4d1	13	11	48	23	W3M	901361	3291.9	436.3	197.8	43.7						-62.6	-40.1	-33.4	-29.7	-34.0	
	C6	6	12	48	23	W3M	916700	3400.0	400.0	0.0	0.0	0.0					-62.5	-40.9	-35.6	-23.8	-35.7	-40.9
	B5	5	12	48	23	W3M	920300	3400.0	400.0	0.0	0.0	0.0					-62.8	-40.6	-35.0	-29.9	-33.8	
	b5	5	12	48	23	W3M	920877	3050.7	358.2	145.0	34.7						-63.0	-41.7	-35.8	-31.1	-36.0	-18.5
	c6	6	12	48	23	W3M	951440	3127.0	362.6	150.1	34.0						-61.4	-41.4	-37.6	-34.2	-39.6	
	C4	4	12	48	23	W3M	965320	3058.2	387.6	162.0	42.2						-63.7	-41.6	-35.8	-30.7	-35.0	
	c	5	14	48	23	W3M	974766	3650.0	355.5	68.4	30.1						-63.9	-40.0	-33.7	-29.9	-32.4	-6.6
	c	5	14	48	23	W3M	974766	3650.0	355.5	30.1	11.7	10.1			5.4		-63.9	-40.0	-33.7	-29.9	-32.4	-6.6
19.09.1999	2D1	13	11	48	23	W3M	978195	4209.5	490.8	76.7	36.0						-64.8	-41.1	-34.2	-28.0	-29.3	
		2	27	49	22	W3M	547327	1441.0	108.6	25.0	7.7	2.8					-68.2	-42.6	-40.4	-33.2	-37.2	
	a	11	18	49	22	W3M	669648	2101.1	140.1	38.0	10.9	23.3					-65.0	-41.8	-41.0	-31.9	-21.1	-34.7
15.05.2002	a	15	22	49	22	W3M	733337	1840.2	111.1	29.5	6.1						-67.4	-43.7	-39.6	-32.5	-34.6	-16.9
	##	2	27	49	22	W3M	952332	2639.2	184.6	49.1	11.7						-68.9	-43.1	-41.3	-35.0	-38.6	-14.5
	A15	15	22	49	22	W3M	977633	2485.7	173.9	39.3	11.0						-68.3	-43.7	-41.2	-34.1	-37.5	-29.7
	##	8	28	49	22	W3M	982917	2547.7	171.1	39.2	11.2						-66.9	-42.5	-41.1	-34.4	-35.9	-34.6
	c4	4	16	49	26	W3M	772802	2618.5	263.1	98.4	24.3						-60.4	-41.1	-36.6	-33.4	-34.5	
		1	21	51	23	W3M	556927	669.2	89.4	55.2	7.4						-71.8	-55.0	-42.6	-36.3	-41.4	
	a	3	20	51	24	W3M	587284	1007.4	99.2	26.8	8.0	3.7					-64.5	-52.2	-42.4	-33.3	-35.7	-10.2
	A9	9	12	51	24	W3M	603600	1000.0	100.0	0.0	0.0	0.0					-66.2	-52.5	-40.5	-32.6	-34.8	
	a	9	12	51	24	W3M	705771	1173.8	121.5	38.5	11.2	24.2					-69.9	-54.7	-41.6	-33.2	-35.8	-22.0
		3	20	51	24	W3M	724767	1370.0	122.3	38.3	10.8	25.2					-68.0	-51.9	-41.9	-33.6	-25	-24.5
		9	12	51	24	W3M	729299	1198.0	121.1	37.1	10.5	29.5					-72.6	-54.7	-41.1	-33.0	-30.6	-25.8
		9	12	51	24	W3M	872413	1294.9	140.4	36.3	10.2						-67.4	-54.3	-41.4	-33.4	-36.9	-26.7
	A3	3	20	51	24	W3M	908900	1700.0	100.0	0.0	0.0	0.0					-70.2	-50.5	-40.8	-32.5	-36.2	
	a9	9	12	51	24	W3M	948388	1319.5	135.7	93.0	12.1						-68.6	-55.2	-41.7	-34.0		
	a3	3	20	51	24	W3M	976713	1565.3	158.1	95.3	12.3						-63.6	-50.2	-40.4	-32.8	-37.9	-24.3
	a1	1	21	57	23	W3M	556927	669.2	89.4	55.2	7.4						-71.8	-55.0	-42.6	-36.3	-41.4	
18.04.2004		6	19	23	21	W4M	987000	4000.0	1000.0	100.0							-54.3	-43.5	-31.5	-27.0	-29.7	
		1	33	42	1	W4M	855140	6837.0	712.8	133.4	68.9	32.9					-61.5	-31.5	-28.8	-26.5	-26.3	
		16	24	44	1	W4M	960388	4322.0	313.1	68.9	22.4						-65.1	-37.9	-34.6	-21.4	-31.7	-26.6
	c	6	19	46	6	W4M	785418	4757.0	980.0	177.4	115.9						-63.4	-37.1	-29.3	-27.0	-27.3	
	11c	11	29	46	6	W4M	952945	3849.4	662.5	303.2	74.7						-65.2	-41.5	-32.6	-29.1	-29.9	
17.07.2003	A	7	11	47	5	W4M	667148	2118.0	196.1	46.9	19.6	18.4					-63.6	-46.7	-39.0	-33.6	-35.2	
	1c	1	36	47	5	W4M	954117	2439.7	264.9	126.4	26.2						-63.3	-48.6	-41.2	-33.2	-37.4	
		7	11	47	5	W4M	978305	3794.6	357.0	68.6	29.8						-64.5	-48.1	-41.2	-33.0	-38.0	
		10	17	48	5	W4M	981200	3382.2	350.4	69.9	35.2						-65.1	-50.2	-41.4	-35.1	-35.3	
		10	5	49	6	W4M	951052	2369.0	268.9	171.8	28.3						-64.4	-50.4	-42.0	-33.3	-37.5	
	10d	10	4	50	6	W4M	972109	2704.2	260.0	146.7	28.1						-65.5	-49.8	-40.9	-34.9	-26.2	
		10	4	50	6	W4M	973170	3065.1	308.3	173.1	33.5						-66.3	-47.4	-39.6	-31.8	-39.8	-18.0
	15a	15	22	54	2	W4M	571291	993.5	86.6	50.2	6.7						-70.5	-53.2	-43.2	-33.8	-37.1	
16.04.2000	6b	6	21	54	5	W4M	807240	1998.8	222.9	94.5	20.2						-62.8	-48.6	-41.0	-33.3	-36.8	-51.9
	16D	16	32	55	4	W4M	980321	4113.5	343.5	44.8	19.5	7.2					-61.9	-41.0	-33.8	-29.0	-31.2	-11.3
12.10.2004	c	5	18	61	3	W4M	748966	2111.0	183.0	25.0	16.0						-60.6	-44.0	-35.6	-31.3	-33.8	-6.4
	10d	10	36	62	7	W4M	989423	4032.7	420.8	91.2	32.6						-62.4	-45.5	-40.3	-32.5	-37.3	-38.5
27.04.1998		9	23	63	3	W4M	975304	470.5	2.2	0.0	0.1						-66.4	-36.3				-1.3

Appendix 2. Soil gases from the University of Alberta database - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Date	UWI						C_1	C_2	C_3	C_4	C_5	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$^{13}C_{iC4}$	$^{13}C_{nC4}$	$^{13}C_{CO2}$
16.10.1999		12	10	40	4	W3M	1618	12.0	5.8	1.4	9.6						-57.5	-26.7	-24.7	-25.0		-27.6
12.06.1998		12	10	40	4	W3M	7278	11.8	96.7	52.0	104.9						-36.9	-35.7	-21.6	-24.6	-23.9	-23.4
21.09.2000	a14	14	19	49	16	W3M	14690	28.1	1.2	0.3	0.0						-41.0	-45.5	-38.1			-24.6
19.12.2003	b6	6	16	48	18	W3M	36200	52.6	2.6	0.9	0.1	1.2		63.4	36.5		-67.4	-47.9	-37.7			-41.0
09.01.2004	b	6	16	48	18	W3M	36200	52.6	2.6	0.9	0.1	1.2					-67.4	-47.9	-37.7			-41.0
04.06.2004		1	19	21	19	W3M	522725	1110.0	90.0	29.0	6.4	3.7					-69.1	-58.3	-44.6	-29.9		-52.4
07.07.1998	a3	3	17	48	19	W3M	151060	156.2	11.5	6.5	2.1						-54.6	-36.7	-34.4	-27.8	-31.9	-75.8
12.09.2000	a9	9	17	48	19	W3M	221772	471.2	43.3	20.3	3.9	13.7					-65.5	-38.3	-34.4			-48.3
07.07.1998	a4	4	17	48	19	W3M	92098	77.7	5.4	7.1	1.4						-53.3	-36.6	-33.2			-77.8
12.05.2004	a11	11	18	48	19	W3M	79707	104.7	11.7	9.7	0.7						-66.8	-43.9	-38.1	-38.4	-29.0	-24.4
14.09.2004		1	18	48	19	W3M	211140	323.4	37.8	12.2	3.3	2.0					-62.3	-46.3	-40.7	-33.3		-37.9
12.09.2000	a11	11	18	48	19	W3M	14918	23.7	2.6	0.6	0.3						-64.8					-30.5
09.07.2004	a	4	19	48	19	W3M	821384	1611.0	73.7	18.7	5.7	117.4					-67.8	-40.5	-38.0	-31.4	-33.0	-70.8
17.07.2003	a13	13	19	48	19	W3M	177552	436.8	47.4	13.9	5.2	2.1		103.5	80.4		-64.7	-41.8	-37.6	-25.5	-20.4	-29.2
18.09.2003	a13	13	19	48	19	W3M	663627	1629.0	184.0	51.5	25.7						-64.7	-41.8	-37.6	-25.5	-20.4	-29.2
12.09.2000	a11	11	20	48	19	W3M	39900	124.7	20.4	13.5	16.3	1040.0					-66.1	-41.2				-29.2
20.08.2003		10	21	48	19	W3M	262216	549.4	41.6	10.3	3.6						-63.8	-39.4	-35.9	-30.4	-22.9	-35.7
18.05.2000		7	22	48	19	W3M	146166	275.3	22.6	6.2	2.4		184				-67.0	-43.4	-35.0	-30.3	-29.2	-12.1
28.05.2001		7	22	48	19	W3M	48105	53.5	2.6	0.7	0.2			11.9	23.8		-65.4	-39.5	-34.3			-33.4
22.08.2001	14c	14	28	48	19	W3M	475193	1050.9	95.2	33.5	6.7		51242				-60.9	-41.4	-38.2	-33.0	-29.2	-52.3
17.05.2000	14c	14	28	48	19	W3M	68510	42.2	6.9	5.0	1.3		84				-49.9	-38.1	-35.8	-30.4	-35.7	-41.9
22.08.2001	14c	14	28	48	19	W3M	1742	3.7	0.4	0.2	0.1		1186				-61.4					-17.2
22.09.2000	a7	7	30	49	19	W3M	859279	1494.0	180.0	106.4	13.5	4.4					-60.6	-43.4	-39.5	-34.4	-37.3	
04.06.2004		1	33	21	20	W3M	850456	1678.6	126.4	51.6	10.3	8.3					-68.0	-57.7	-43.9	-30.4	-38.2	-43.3
30.07.2003		13	9	48	20	W3M	32355	95.5	7.0	2.4	0.1			136.3			-71.4	-48.7	-37.7	-26.4		-13.5
22.09.2000	a4	4	19	48	20	W3M	355202	623.2	60.0	37.5	4.8						-69.3	-49.0	-41.0	-32.2	-36.5	-9.5
19.12.2003		4	19	48	20	W3M	149217	247.0	11.5	3.4	0.6	1.2		107.5	2.9		-53.1	-34.1	-33.3	-30.3	nm	-57.1
22.07.2003		4	19	48	20	W3M	174630	425.5	28.8	9.0	1.9	1.0		93.8	22.0		-56.7	-36.7	-36.1	-30.1	-20.3	-50.8
04.09.2003		4	19	48	20	W3M	135086	297.2	24.5	7.9	2.1	15.4		66.5	0.6		-58.7	-37.6	-37.1	-30.0	-20.2	-51.9
12.05.2004	a	5	19	48	20	W3M	13868	49.4	7.3	2.8	0.8	4.8					-53.8	-42.7	-37.0	-29.7		-51.5
22.09.2000	d11	11	19	48	20	W3M	156081	614.7	70.7	51.8	6.1	10.1	40973				-59.5	-46.3	-39.7	-29.4	-29.2	-32.4
18.09.2003		4	19	48	20	W3M	372915	983.5	73.2	21.3	5.7						-59.4	-37.7	-38.6			-51.0
22.09.2000	a4	4	19	48	20	W3M	5436	10.8	2.0	0.6	0.8						-50.0	-46.5				-28.0
22.09.2000	a4	4	19	48	20	W3M	5436	10.8	2.0	0.6	0.8						-50.0	-46.5				-28.0
12.09.2000	a10	10	36	48	20	W3M	25371	47.4	6.2	1.7	0.5						-57.8	-42.9				
11.09.2000	a5	5	7	49	20	W3M	66537	121.4	16.8	5.4	1.5	4.6					-69.8	-46.1	-37.9			-36.1
11.09.2000	a5	5	7	49	20	W3M	66537	121.4	16.8	5.4	1.5						-69.8	-46.1	-37.9			-36.1
11.09.2000	a4	4	7	49	20	W3M	105810	219.6	35.6	25.4	2.6						-55.7		-37.8			-24.3
28.09.1999		15	30	47	21	W3M	41481	81.7	6.9	2.4	1.9		6637				-60.0	-42.8	-35.1	-28.2		-54.0
05.07.2003		4	28	48	21	W3M	109100	206.0	17.0	7.7	1.1						-50.1	-37.5	-34.5	-29.1	-27.2	-41.8
05.07.2003		4	28	[illegible]	[illegible]	W3M	109100	206.0	17.0	7,7	1.1	170.3			1.4		-50.1	-37.5	-34.5	-29.1	-27.2	-41.8
05.07.2003		4	28	48	21	W3M	179068	370.9	25.6	10.2	1.1						-52.6	-39.0	-34.8	-28.4	-27.6	-42.8
05.07.2003		4	28	48	21	W3M	179068	370.9	25.6	10.2	1.1	150.4			2.4		-52.6	-39.0	-34.8	-28.4	-27.6	-42.8
05.05.2004	c	2	1	48	22	W3M	8235	15.2	5.5	3.4	1.3	3.7					-25.6	-32.7	-32.1	-27.5	-34.1	-55.6
14.09.2000	a12	12	16	49	22	W3M	298850	911.7	86.9	28.4	7.0						-62.9	-41.8	-39.8	-35.1	-31.2	-38.8
14.09.2000	a5	5	16	49	22	W3M	792003	2721.0	273.2	99.7	24.6						-63.0	-40.8	-36.0	-34.1	-27.1	-59.6
16.05.2002		11	22	49	22	W3M	239877	576.0	45.0	16.2	3.1	13.8					-56.7	-40.6	-39.2	-31.9	-30.2	-68.9
15.05.2002	a	15	22	49	22	W3M	225349	616.5	50.2	16.6	4.2	4.0					-57.7	-39.2	-37.8	-31.6		-39.0
27.06.2003		10	22	49	22	W3M	101379	195.4	12.0	3.7	0.9	0.3		1.4			-60.4	-43.0	-38.3	-31.3		-45.7
27.09.2002		10	22	49	22	W3M	114111	244.0	16.0	4.4	1.3						-74.9	-46.0	-39.6	-30.8		-23.8
16.05.2002		10	22	49	22	W3M	330	15.2	4.6	2.8	1.7	102.3					-31.0	-43.2	-45.8	-29.0	-23.0	-31.8
13.08.2001	a16	16	22	49	22	W3M	8126	23.6	2.0	0.5	0.2											-30.3
13.08.2001	a	13	25	49	22	W3M	21522	52.4	2.9	0.9	0.3	8.7					-62.5	-41.9	-37.0	-36.9		-34.6
20.08.2004	a	7	27	49	22	W3M	162945	529.7	50.7	10.0	3.0	10.5		0.5			-53.0	-36.9	-37.7	-33.2		-54.0
11.06.2003		16	27	49	22	W3M	155169	385.7	26.9	7.0	1.7						-68.5	-43.7	-38.7	-33.1		
18.11.2003		10	27	49	22	W3M	893256	2357.0	202.0	53.0	17.9	12.5			22.6		-65.2	-41.8	-39.7	-32.9	-23.2	
19.11.2003		3	27	49	22	W3M	192515	474.6	40.0	10.9	4.0				1.9		-63.0	-41.1	-39.2	-32.4	-35.8	
18.07.2002		9	27	49	22	W3M	170273	625.1	51.1	15.5	3.7						-54.1	-37.5	-37.4	-32.3	-22.6	-66.0
18.11.2003		9	27	49	22	W3M	262595	729.9	66.7	18.2	6.3						-60.5	-40.0	-37.9	-31.8	-34.3	
08.09.2000	a5	5	27	49	22	W3M	679233	3264.1	477.7	279.3	9.5						-65.2	-36.7	-28.3	-29.4	-22.4	-27.2
23.06.2003		5	27	49	22	W3M	697741	3386.0	469.3	129.6	10.1	17.2					-66.2	-37.8	-27.6	-28.7		-54.8
16.05.2002	a	2	27	49	22	W3M	175877	210.7	7.9	4.3	0.3	10.5					-51.9	-37.4	-37.1	-28.4	-24.0	-50.5
08.09.2000	a7	7	27	49	22	W3M	292814	721.5	56.5	28.2	3.6						-67.0	-42.9	-40.5	-27.7		-23.0
08.09.2000	a5	5	27	49	22	W3M	246117	1160.7	165.8	103.7	3.2						-61.9	-36.3	-27.3	-26.6		-44.3
08.09.2002	a16	16	27	49	22	W3M	602860	1631.5	130.2	68.7	9.1						-66.7	-42.5	-41.0			-29.1
08.08.2002		3	27	49	22	W3M	8590	29.1	1.8	0.5	0.1				1.6		-61.8	-39.3	-39.5		-20.9	-33.0
08.09.2000	a6	6	27	49	22	W3M	11562	21.0	2.4	0.1	0.1						-57.5		-34.8			-33.3
18.07.2002		1	27	49	22	W3M	7226	19.7	1.7	0.5	0.1	5.7			1.9		-66.1	-40.8				-46.5
08.09.2000	a16	16	27	49	22	W3M	4167	11.1	0.9	0.2	0.1						-62.1					-37.8
08.09.2000	a12	12	27	49	22	W3M	3506	14.2	2.0	0.5	0.1						-60.0					-23.0
08.09.2000	a7	7	27	49	22	W3M	520288	1578.8	138.1	76.8	9.9						-59.0					
24.07.2001	9a	9	28	49	22	W3M	203569	346.6	21.9	5.9	1.1				5.0		-61.8	-40.9	-39.3	-31.9	-28.1	-79.7
15.05.2005		8	28	49	22	W3M	12395	43.6	2.1	0.8	0.1	7.8			702.5		-51.7	-32.1				-25.9
25.07.2001	a13	13	35	49	22	W3M	21552	52.4	2.9	0.9	0.3	8.7			7.9		-62.5	-42.0	-37.0	-36.9		-36.6
15.05.2001		13	35	49	22	W3M	13547	71.5	7.7	3.6	1.3	14.1			511.1		-62.6	-39.5	-38.1	-31.5	-26.9	-28.8
13.09.2000	a1	1	35	49	22	W3M	433377	1096.7	109.1	57.3	6.4						-65.2					-39.1
11.06.2003		13	35	49	22	W3M	20533	71.2	1.4	0.3	0.1	0.6					-72.3	-40.1				-25.5
14.02.2000		11	26	13	23	W3M	812902	2204.0	295.8	86.6	34.1	21.1					-66.7	-57.2	-40.8	-31.1	-34.5	-21.3
14.02.2000		2	26	13	23	W3M	297833	751.2	66.1	25.1	5.8	16.0					-62.0	-59.2	-43.9	-30.9	-34.2	-44.1
25.10.2002		2	2	31	23	W3M	45519	106.4	5.5	2.6	0.4	3.9			1.4		-72.7	-51.5	-43.8	-33.8	-28.8	-63.6
13.11.2003		2	2	31	23	W3M	156752	42.5	3.3	1.5	0.6	4.0			5.1		-52.0	-53.9				-21.1
18.08.2000		14	28	31	23	W3M	2717	28.3	14.9	23.1	12.0						-50.0	-35.3	-27.3	-30.0	-29.0	-29.7
20.11.2000	7c	12	36	45	23	W3M	5612	14.1	1.8	0.3	0.4						-61.0					-12.2

Appendix 2. Soil gases from the University of Alberta database - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

(cont.)

Date	UWI						C_1	C_2	C_3	C_4	C_5	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$^{13}C_{C4}$	$^{13}C_{nC4}$	$^{13}C_{CO2}$
17.11.2000	5c	7	3	46	23	W3M	100202	196.5	23.6	4.3	1.5						-56.4	-46.6	-38.6	-31.4	-35.4	-19.2
19.07.2000	a1	1	6	47	23	W3M	397812	1283.9	155.0	54.8	14.3	5.8	79563		23.3		-57.3	-40.6	-35.1	-29.7	-35.3	-55.4
24.08.2001	a16	16	17	47	23	W3M	10129	25.3	1.8	0.2	0.1		12782				-46.7	-36.4	-33.1			-54.7
24.08.2001	a16	16	17	47	23	W3M	30909	82.3	5.2	0.5	0.2		24046				-49.0	-37.6	-32.8			-56.1
23.06.2003		10	24	47	23	W3M	364233	987.1	100.6	20.2	9.9	41.7					-63.2	-42.4	-35.4	-29.3		-29.6
31.07.2000	a9a	9	3	48	23	W3M	31270	115.4	19.6	8.2	1.9						-44.5	-33.0	-31.0	-29.0	-30.1	-38.9
28.10.2000		2	8	48	23	W3M	382976	1027.1	108.6	42.3	9.1						-64.0	-38.5	-33.2	-29.6	-27.9	-58.1
31.07.2000	a9a	9	10	48	23	W3M	15121	57.8	11.5	4.3	1.2	11.7	–				-45.8	-39.2	-35.7	-32.6	-28.9	-30.5
01.08.2000	4c1	12	11	48	23	W3M	120637	449.9	63.2	30.9	7.7	7.6	1451				-62.0	-40.5	-38.7	-35.5	-41.1	-21.4
01.08.2000	24/1	13	11	48	23	W3M	723455	2259.3	90.9	98.7	6.6	12.6					-63.8	-39.7	-35.2	-35.0		
02.08.2000	d10	10	11	48	23	W3M	98869	280.4	31.5	11.7	2.8	8.7	17796				-64.6	-42.5	-38.1	-34.5	-33.6	-45.3
05.10.2000	2D8	8	11	48	23	W3M	96782	352.1	51.0	24.8	6.9	3.8	2903				-63.7	-42.6	-38.8	-34.1	-38.1	-33.2
08.08.2000	b7	7	11	48	23	W3M	30249	117.3	24.2	6.4	4.1						-68.9	-44.1	-36.7	-33.7	-39.1	-14.5
02.08.2000	b9	9	11	48	23	W3M	657473	2018.1	220.9	100.8	23.5	24.5	423				-65.2	-41.8	-36.6	-32.7	-37.9	-10.8
26.07.2000	a10	10	11	48	23	W3M	648334	1940.9	222.1	84.5	20.4	7.9					-63.0	-41.1	-36.9	-32.4	-35.3	-39.0
02.08.2000	d9	9	11	48	23	W3M	408645	1295.0	143.0	59.0	13.0	4.3					-67.3	-42.8	-38.0	-32.2	-35.0	-15.7
29.09.1999	2B1	13	11	48	23	W3M	59595	99.2	6.5	2.4	0.7	3.2					-68.4	-41.4	-34.3	-31.0		-34.6
13.07.2001	2D1	13	11	48	23	W3M	738765	2618.0	283.3	59.9	23.6		1144				-60.7	-39.1	-33.7	-30.6	-35.8	-44.7
26.07.2000	2d8	8	11	48	23	W3M	311303	961.0	117.5	49.4	12.7		173				-67.3	-43.1	-36.7	-30.5	-34.0	-4.6
23.08.2001	2B1	14	11	48	23	W3M	80269	188.2	20.0	5.6	1.9		155688				-63.5	-42.6	-34.2	-30.4	-31.5	-41.1
31.08.2000	4d1	13	11	48	23	W3M	136184	389.0	57.3	25.9	4.2		65368				-56.2	-40.6	-32.2	-29.6		-49.2
02.08.2000	c16	16	11	48	23	W3M	88953	259.1	29.7	9.7	3.1		3558				-67.2	-42.3	-34.3	-29.4	-35.6	-26.6
29.09.1999	A10	10	11	48	23	W3M	386059	1225.8	128.5	21.8	11.0	34.3					-66.4	-42.2	-33.8	-29.4		-3.7
31.07.2000	d15	15	11	48	23	W3M	75644	176.3	30.0	14.3	4.1	174.6					-59.5	-39.8	-32.6	-29.3	-34.8	-15.9
08.08.2000	a8	8	11	48	23	W3M	267776	296.5	10.0	12.2	1.4	12.8					-70.4	-45.6	-31.5	-28.8	-26.6	-27.5
19.09.1999	2D1	13	11	48	23	W3M	954849	3630.6	422.2	66.1	31.0		439				-64.3	-41.1	-34.5	-28.6	-32.2	9.6
02.08.2000	a14	14	11	48	23	W3M	523241	1485.5	154.8	63.9	12.8	3.7					-65.6	-41.8	-35.6	-27.4	-32.9	-31.0
30.09.1999	2B1	14	11	48	23	W3M	56130	121.4	12.5	3.1	1.7	7.3	26942				-74.3	-45.9	-37.2	-27.2		-49.8
08.08.2000	d8	8	11	48	23	W3M	253643	573.8	86.0	279.8	70.5	722.4	9385				-66.8	-40.1	-30.6	-24.7	-23.4	-26.0
29.09.1999	2C1	10	11	48	23	W3M	29513	74.5	57.9	277.6	136.3	1258.0					-59.9	-38.1	-23.9	-24.6	-23.1	-1.8
30.07.2003	A	6	11	48	23	W3M	29083	124.8	7.9	5.6	1.2	92.5					-47.2	-33.9	-31.8	-24.5		-28.9
08.08.2000	b10	10	11	48	23	W3M	100092	304.5	49.7	116.5	22.5	170.4					-63.4	-39.9	-31.9	-24.4	-22.1	-15.0
08.08.2000	d7	7	11	48	23	W3M	285765	769.2	87.8	15.4	7.4	4.9					-68.4	-43.6	-37.9	-21.3	-38.2	-45.6
02.08.2000	c10	10	11	48	23	W3M	41183	48.4	15.5	115.5	58.1	1174.2					-57.8		-29.0	-20.2	-22.7	-19.6
01.08.2000	23/1	13	11	48	23	W3M	29252	61.3	5.3	1.1	0.3						-70.2	-43.6	-34.4			-49.1
02.11.2001	2D1	13	11	48	23	W3M	653369	1820.2	162.7	31.9	12.5		64098				-60.7	-38.4	-31.1			-46.6
02.11.2002	2D1	13	11	48	23	W3M	19956	8.6	0.4	0.1	0.1		103713				-53.5					-58.7
08.08.2000	dd1	1	11	48	23	W3M	39637	28.2	0.5	0.2	0.2		9117				-74.0	-47.3				-38.0
29.09.1999	A8	8	11	48	23	W3M	17497	16.1	0.6	0.5	0.2	13.8					-64.7	-50.0				-37.7
13.07.2001	2d8	8	11	48	23	W3M	1114	6.8	0.8	0.2	0.2		379				-67.7					-7.5
27.07.2000	b3	3	12	48	23	W3M	44229	131.1	15.2	3.8	0.8		55729				-53.7	-38.2	-37.8	-35.8	-36.2	-38.8
31.07.2000	c4	4	12	48	23	W3M	351007	965.5	108.6	40.2	8.3						-65.3	-41.7	-37.1	-33.0	-39.1	-29.0
23.07.1998	B11	11	12	48	23	W3M	65208	10.9	0.9	0.4	0.4		56600				-74.4	-43.8	-36.7	-32.1		-51.0
27.07.2000	a3	3	12	48	23	W3M	865691	2847.9	324.1	136.7	28.0	6.0					-65.0	-41.3	-36.0	-31.4	-35.5	-38.2
01.08.2000	c5	5	12	48	23	W3M	205577	658.4	80.6	34.4	8.7	6.5					-64.3	-41.5	-35.7	-31.4	-32.7	-48.9
01.08.2000	d5	5	12	48	23	W3M	38310	113.5	25.3	29.3	7.4	103.0	16090				-62.5	-39.2	-35.9	-31.1	-31.8	-31.1
27.07.2000	b4	4	12	48	23	W3M	72880	199.4	22.6	8.6	2.0	0.0					-65.0	-42.0	-37.9	-31.0	-32.3	-67.4
01.08.2000	c6	6	12	48	23	W3M	98122	295.7	37.6	8.2	4.7	12.0					-68.8	-43.8	-36.0	-30.9	-36.4	-24.4
27.07.2000	c11	11	12	48	23	W3M	45200	117.9	11.7	3.6	1.3						-64.7	-43.3	-37.0	-30.5	-33.1	-14.0
01.08.2000	b5	5	12	48	23	W3M	417748	1280.2	146.3	59.7	14.3	5.4					-65.3	-41.7	-35.4	-30.4		-34.7
01.08.2000	b13	13	12	48	23	W3M	67097	178.6	21.9	6.7	2.3	4.7					-69.0	-44.2	-35.0	-30.3	-29.5	-36.8
23.07.1998	C11	11	12	48	23	W3M	43100	0.0	0.0	0.0	0.0	0.0					-56.3	-40.4	-34.4	-29.8	-35.8	
01.08.2000	b12	12	12	48	23	W3M	59706	33.1	14.6	241.6	49.0	233.6	41794				-66.8	-31.8	-25.5	-24.4	-21.4	-18.5
27.07.2000	c3	3	12	48	23	W3M	99135	114.0	6.3	1.4	0.4		3965				-74.3	-47.1	-36.6	-24.3	-32.7	-26.5
23.07.1998	B12	12	12	48	23	W3M	134900	600.0	200.0	300.0	200.0	8800.0					-59.3	-36.9	-26.1	-22.2	-17.3	-26.1
27.07.2000	a4	4	12	48	23	W3M	27198	64.3	5.9	1.2	0.3						-66.0	-35.5	-38.6			-26.0
27.07.2000	b11	11	12	48	23	W3M	28300	0.0	0.0	0.0	0.0		12390				-78.1	-37.1				-19.4
08.07.2003	A	7	14	48	23	W3M	28291	93.5	8.2	2.1	1.1	6.1			2.2		-70.2	-43.6	-36.4	-31.8		-42.2
26.07.2000		10	14	48	23	W3M	201775	598.0	75.0	35.8	8.6	8.5					-69.0	-42.3	-35.5	-31.8	-34.5	-29.3
08.07.2003		3	14	48	23	W3M	137058	384.6	40.7	9.3	4.1	8.9			1.7		-71.1	-43.7	-36.3	-31.7	-29.9	-48.9
04.08.2000	c6	6	14	48	23	W3M	210381	869.1	137.4	88.5	19.1	112.8	5260				-62.1	-41.5	-36.5	-30.9	-35.2	-11.5
08.07.2003		15	14	48	23	W3M	338271	1042.0	96.7	22.1	9.7	12.6			11.4		-68.4	-39.8	-33.7	-30.7	-29.3	-36.8
20.07.2000	c11	11	14	48	23	W3M	22810	257.4	143.0	94.0	25.9	125.4	32847				-41.0	-34.1	-32.8	-30.7	-36.3	-18.9
20.07.2000	c12	12	14	48	23	W3M	36970	155.3	30.3	13.4	4.2	63.0	41884				-59.1	-40.4	-34.7	-30.7	-35.8	-35.6
08.06.1998	D6	6	14	48	23	W3M	524700	1800.0	100.0	0.0	0.0	1700.0					-61.6	-39.6	-33.5	-30.6		
08.07.2003	A	4	14	48	23	W3M	28123	126.4	18.8	5.9	2.9	6.1			8.8		-68.1	-41.6	-36.0	-29.8		-29.5
08.06.1998	C6	6	14	48	23	W3M	129700	1000.0	100.0	0.0	0.0	56800	56800				-56.2	-39.4	-34.4	-29.6	-33.9	-30.6
10.10.2000	c12	12	14	48	23	W3M	41511	1463.7	171.8	67.4	15.2	96.8	7887				-57.2	-39.6	-32.9	-28.9	-33.8	-35.5
04.08.2000	d6	6	14	48	23	W3M	12741	93.7	39.6	32.5	12.0	441.2					-50.6	-37.2	-31.7	-28.7	-31.1	-24.3
04.08.2000	c5	5	14	48	23	W3M	240722	853.9	124.3	58.5	16.2	25.2					-65.4	-41.2	-33.8	-28.7	-34.1	-14.3
20.07.2000	c12	12	14	48	23	W3M	403095	1353.2	169.9	64.4	14.4	178.0	100774				-55.5	-37.9	-31.8	-27.5	-33.1	-30.3
27.07.2000	a2	2	14	48	23	W3M	11776	37.5	2.8	5.0	4.1						-58.7	-20.4	-15.5	-24.8		-24.4
04.08.2000	d6	6	14	48	23	W3M	89683	371.3	105.6	72.6	22.5	505.2					-63.4	-40.1	-32.3	-24.1	-30.2	-0.7
02.07.1997	A11	11	14	48	23	W3M	28000	200.0	0.0	0.0	0.0	34300					-68.5	-41.9	-34.9			-27.8
08.06.1998	C10	10	14	48	23	W3M	296800	900.0	100.0	0.0	0.0	30200					-57.7	-38.4	-33.4			-36.2
20.07.2000	A	10	16	48	23	W3M	587028	2265.0	391.0	191.0	40.0						-63.1	-37.8	-30.9	-28.3	-30.4	-24.8
20.07.2000	a10	10	16	48	23	W3M	962897	4093.0	744.4	371.6	77.6	16.3					-61.9	-41.1	-30.9	-28.3	-30.8	-15.9
16.10.2001	A	11	16	48	23	W3M	39846	87.7	7.2	2.1	3.5	13.1			3.2		-75.5	-43.8	-33.7	-27.9	-25.5	-16.3
20.10.2001	b	6	19	48	23	W3M	35529	228.9	55.9	23.9	14.1	28.9			4.3		-86.6	-32.5	-27.1	-25.4	-25.6	-91.6
17.10.2001	d	15	19	48	23	W3M	40031	144.3	8.1	3.3	0.9						-63.0	-36.4	-29.8	-25.3	-26.8	-35.8
16.10.2001	a	16	21	48	23	W3M	267619	1302.9	211.0	49.6	22.4	12.2			0.3		-65.1	-37.0	-30.4	-28.5	-28.4	-24.3
16.10.2001	a	8	21	48	23	W3M	4109	36.2	7.9	3.8	2.1	10.9			41.9		-54.6	-36.2	-30.5	-28.0	-20.8	-40.2
17.10.2001	a	9	21	48	23	W3M	58527	272.5	15.8	5.3	2.0						-63.2	-35.9	-29.1	-27.7	-29.3	-41.1
01.06.2000	a6	6	21	48	23	W3M	64848	343.7	15.1	27.3	0.6	–					-51.9	-32.8	-21.8	-27.5	-32.1	-60.4

Appendix 2. Soil gases from the University of Alberta database - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

(cont.)

Date	UWI						C_1	C_2	C_2	C_2	C_3	C_{4+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$^{13}C_{C4}$	$^{13}C_{nC4}$	$^{13}C_{CO2}$
16.10.2001	a	14	21	48	23	W3M	33843	155.0	26.2	7.4	5.6	21.2					-65.3	-46.6				-45.7
24.07.2001	a10	10	22	48	23	W3M	262954	549.0	39.2	9.3	2.3				2.4		-71.6	-45.4	-41.8	-34.6	-28.2	-18.0
19.07.2000	a10	10	22	48	23	W3M	151063	1008.0	319.0	274.7	70.7		6214				-61.0	-37.7	-30.4	-27.9	-29.8	-2.0
20.07.2000	b14	14	29	48	23	W3M	227530	795.5	133.3	78.5	17.4	5.7					-61.1	-36.2	-29.9	-28.8	-31.4	-53.9
04.08.2000	d7	7	29	48	23	W3M	12614	77.2	13.6	4.8	1.7						-52.8	-31.6	-27.9	-27.4	-29.2	-48.8
01.11.2002	b	6	29	48	23	W3M	102819	916.7	187.9	69.5	43.2	71.3		0.2	3.7		-44.2	-28.1	-25.1	-26.2	-26.9	-16.9
19.07.2000	b2	2	29	48	23	W3M	3769	16.4	2.3	0.5	0.2	2.3					-55.7	-30.0				-23.7
20.11.2002	b	2	31	48	23	W3M	25939	73.5	5.1	4.8	0.6						-48.9	-25.8	-13.1	-22.1	-26.8	-20.0
31.08.2000	a2	2	36	48	23	W3M	422418	1159.1	132.7	54.2	11.5						-65.2	-40.4	-34.1	-29.4	-33.0	-50.0
03.05.2004	a	1	22	49	23	W3M	146380	271.2	23.0	6.9	1.8	1.0					-69.0	-45.6	-40.8	-32.3	-33.3	-57.5
05.05.2004	a	4	23	49	23	W3M	11706	58.7	4.6	1.4	0.4	2.8					-52.0	-38.1	-36.6	-30.4		-46.9
06.09.2000	a	1	21	51	23	W3M	202634	268.0	39.0	22.0	3.0		62817				-81.0	-57.5	-41.0	-34.3	-38.3	-63.6
19.06.2002	a	1	21	51	23	W3M	15225	4.0	2.4	0.8	0.2						-52.1	-47.9	-38.7			-59.7
11.11.2002	c	13	3	52	23	W3M	31294	96.3	6.1	3.0	0.6	10.4		0.6			-57.8	-39.3	-27.2	-22.6		-45.5
03.11.2002	a	1	33	31	24	W3M	10455	75.6	18.8	2.0	1.5	7.4					-14.2					-27.5
04.10.2006		10	36	32	24	W3M	96308	320.0	104.0	18.0	32.0						-82.0	-35.8	-32.9	-31.7	-32.1	-49.2
04.10.2004		8	36	32	24	W3M	74025	367.7	146.0	33.0	45.0						-72.2	-33.5	-30.4	-31.2	-30.6	-20.5
04.10.2005		8	36	32	24	W3M	119770	550.0	200.0	43.0	62.0						-66.5	-30.0	-29.3	-28.7	-29.4	-33.0
06.09.2000	a2	2	2	50	24	W3M	663156	2104.1	214.8	112.7	26.9	7.2					-62.6	-39.7	-36.4	-33.2	-38.5	-19.0
06.09.2000	a7	7	7	50	24	W3M	314998	755.8	80.9	29.6	6.6						-61.1	-42.1	-38.2	-33.9	-40.0	-45.5
13.09.2000	a9	9	12	51	24	W3M	807952	1180.2	124.9	70.2	9.4						-73.9	-55.7	-41.6	-32.0	-33.3	
21.09.2000	a3	3	20	51	24	W3M	249449	418.2	45.8	13.8	4.1		255				-65.2	-50.1	-39.2	-30.1		-23.1
05.10.2000	b1	1	25	48	25	W3M	226068	799.7	76.7	13.0	6.5	4.2					-67.6	-40.5	-33.0	-30.3	-37.6	-44.6
12.06.2003		9	33	51	25	W3M	73307	86.0	6.5	2.2	0.6						-61.7	-48.1	-42.2	-31.2	-29.7	-45.5
22.08.2003	A	10	33	42	26	W3M	1143	15.1	3.5	1.0	0.6				29.3		-64.0	-42.2	-34.6			-17.1
17.10.1999		11	20	47	26	W3M	32823	168.0	24.1	4.6	2.4	1.4					-56.6	-36.2	-29.1	-29.3	-26.7	-20.0
17.10.1999		10	20	47	26	W3M	44152	211.4	31.6	6.0	2.8	1.4					-60.9	-36.8	-31.0	-27.8	-23.3	-15.3
17.10.1999		13	20	47	26	W3M	11308	54.5	3.1	1.5	0.9	2.9					-58.8	-37.1	-32.5	-26.8		-21.5
20.09.2000	a13	13	21	48	26	W3M	26337	97.8	14.8	5.2	1.1						-48.3	-33.5	-28.6	-31.2	-32.5	-35.0
20.09.2000	a13	13	21	48	26	W3M	64594	220.0	31.5	12.9	2.3						-65.2	-38.5	-27.3			-15.9
31.05.1999	A12	12	16	49	26	W3M	415225	1877.1	233.5	69.4	45.8	71.6					-62.3	-41.1	-35.3	-27.8	-33.5	-23.8
14.09.2000	c4	4	16	49	26	W3M	17992	51.7	4.3	0.5	0.3						-56.0	-40.0	-36.7			-34.3
20.09.2000	c8	8	17	49	26	W3M	222499	718.8	68.5	22.8	5.2						-62.2	-42.0	-35.6	-30.7	-34.6	
20.09.2000	a16	16	17	49	26	W3M	101277	354.5	36.7	8.9	2.7						-55.8	-39.9	-35.8	-30.2	-33.1	-60.2
20.09.2000	a9	9	17	49	26	W3M	518847	1520.6	138.2	50.9	11.7						-62.6	-41.3	-35.4	-29.7	-34.5	
22.09.2000	a13	13	19	49	26	W3M	40941	115.6	10.0	2.5	1.0						-55.2	-40.7	-42.6	-29.2		-29.9
Oct 17-02	a	15	17	44	27	W3M	309050	679.4	51.9	11.6	5.2	28.6					-65.2	-39.9	-38.0	-31.5	-22.6	-18.9
05.10.2000	a15	15	17	44	27	W3M	508100	1277.1	104.9	38.7	7.6						-62.3	-38.9	-36.8	-31.3	-26.8	-50.1
24.05.2000	a15	15	17	44	27	W3M	189130	649.2	66.3	32.2	7.5	5.5					-56.7	-35.9	-35.1	-31.2	-34.0	-44.1
25.05.2000	c6	6	18	47	27	W3M	14259	7.0	9.2	7.6	1.3	202.5					-49.8	-34.6	-32.6	-30.6	-34.9	-49.6
21.06.2000	c9	9	18	47	27	W3M	29163	130.0	19.1	4.9	2.0						-61.2	-36.4	-31.3	-29.8	-30.4	-64.1
25.05.2000	a2	2	19	47	27	W3M	226971	1192.4	161.9	78.5	17.2	10.6					-64.7	-37.4	-32.1	-31.0	-38.1	-27.2
11.07.2000	b12	12	22	47	27	W3M	2905	16.9	0.6	4.1	0.1						-59.6	-28.1	-14.2	-30.9	-29.5	
11.07.2000	d3	3	22	47	27	W3M	73289	836.4	319.3	180.4	56.0	37.4					-59.2	-30.3	-27.6	-29.6		-4.0
11.07.2000	a11	11	22	47	27	W3M	99647	596.4	44.6	577.7	117.0	7208.5					-64.2	-28.3	-19.8	-24.9	-25.3	-27.5
23.07.2000		12	28	47	27	W3M	9789	61.0	20.3	9.7	3.0	6.2	9842				-60.0	-38.4	-29.2	-26.4	-26.3	-54.5
23.07.2000	13c	13	30	47	27	W3M	197880	972.8	118.4	37.8	12.1	11.3					-63.0	-38.5	-32.3	-30.2	-34.6	1.2
08.11.1999		4	27	48	27	W3M	114334	462.7	47.3	7.3	4.5	10.0					-61.8	-40.9	-36.3			-23.0
06.10.1999	D1	1	32	48	27	W3M	93296	525.0	76.7	17.1	9.6	11.2					-62.8	-40.8	-33.6	-30.9	-34.9	-15.3
14.09.2000	a7	7	2	49	27	W3M	55995	184.9	7.3	1.2	0.3						-53.6	-37.8	-31.1			-36.1
31.05.1999	D10	10	23	49	27	W3M	99800	215.1	14.2	3.3	0.7	5.4					-60.8	-41.4	-36.2			-57.1
15.11.2001	a	14	12	30	28	W3M	7097	15.6	0.3	0.2	0.1						-61.4	-47.5	-37.9	-31.8	-25.4	-48.1
30.06.2003	10C	14	12	30	28	W3M	12391	26.9	1.8	0.8	0.2	3.4					-66.6	-46.6	-35.7	-28.4	-25.5	-27.7
02.08.2000	a5	5	10	45	28	W3M	118568	180.6	8.3	1.3	0.4		66398				-61.5	-42.0	-28.2			-64.0
19.08.2002	a	10	23	46	28	W3M	[illegible]	1041.8	295.3	88.8	46.8	20.4			1.8		-58.1	-30.1	-26.6	-27.1	-26.8	-71.6
05.10.1999	B1A	1	25	48	28	W3M	226068	799.7	76.7	13.0	6.5	4.2					-52.6	-36.6				-48.3
26.05.2000		6	13	38	1	W4M	113030	1478.6	978.7	362.8	262.2	84.0					-65.0	-35.0		-29.2	-29.1	-43.8
23.05.1997	7A	7	21	38	1	W4M	90900	1900.0	1900.0	500.0	700.0	0.0	58000				-53.4	-30.9	-25.7	-26.6	-26.5	-31.8
31.05.2002		1	29	42	1	W4M	1028	13.5	4.1	3.4	3.0	19.9		14.9			-35.3	-24.1	-31.2	-28.9	-26.5	-23.5
22.07.2003		1	33	42	1	W4M	347736	2980.0	327.1	65.9	31.0	17.6			12.4		-58.7	-29.5	-26.7	-26.3	-26.3	-54.3
01.06.2001		16	24	44	1	W4M	7574	29.9	0.2	1.1	0.1				8.7		-46.1	-25.8				-44.7
12.09.1999	9a	9	27	48	1	W4M	640113	2457.4	246.2	122.2	26.6						-59.3	-43.0	-39.0	-33.7	-37.3	-41.2
27.06.2003	c	6	29	48	1	W4M	683633	751.0	6.6	1.0	0.1	6.8					-65.1	-42.5	-28.8			
11.10.2002	c	6	29	48	1	W4M	352528	405.4	4.0	0.7	0.1						-62.7	-42.4			-19.6	-68.5
23.09.2000	a4	4	19	51	2	W4M	43930	120.2	14.5	6.9	1.5						-44.1	-37.1	-39.9	-36.7	-38.4	-24.3
04.10.1999	15A	15	22	54	2	W4M	426929	763.2	65.1	15.4	4.7						-67.5	-53.3	-42.9	-32.7	-29.8	-14.9
09.05.2002	d	13	24	51	3	W4M	180425	350.2	29.3	7.1	2.3	6.4			149.6		-64.7	-49.4	-39.5			-66.9
09.05.2002	c	13	24	51	3	W4M	49840	86.9	5.5	1.2	0.2	10.3			1.7		-61.5	-46.6	-36.2			-33.1
30.08.2000	7a	7	7	52	3	W4M	123484	1747.3	209.8	50.8	17.8	4.0					-62.1	-48.9	-41.1	-34.4	-39.0	-49.5
11.02.2004	a	8	3	55	3	W4M	1653	0.8		34.2	8.8	5.3					-67.3	-52.5	-41.7	-32.7	-36.5	-43.5
22.10.2001	c	8	27	55	3	W4M	30162	26.2	4.3	4.8	4.2	104.5			7.2		-46.1	-28.7	-24.0	-25.2	-17.0	-31.4
01.11.2002	c	5	27	55	3	W4M	23966	13.0	0.7	0.2	0.3	23.0			54.5		-58.1	-30.4				-33.3
28.08.2002	b	5	33	55	3	W4M	41397	211.5	8.4	1.8	2.6	24.1		61.4	1.4		-48.2	-22.5	-20.5	-23.6		-53.5
08.06.2000	6c	6	5	56	3	W4M	5621	10.6	2.3	1.1	2.0	218.0			10.6		-41.2	-38.4	-32.7	-27.6	-36.2	-26.4
22.07.2003	C	11	6	56	3	W4M	209912	531.7	50.3	8.2	3.1						-55.5	-38.8	-31.9	-26.7		-44.7
22.07.2003	C	11	6	56	3	W4M	32134	114.2	11.0	2.6	0.8						-42.1	-33.5	-28.6			-52.8
12.10.2004	a	12	29	61	3	W4M	5789	42.0	1.0	0.6	0.3						-54.4	-39.4				-23.8
20.09.1999		9	23	63	3	W4M	975510	475.9	2.4	0.1	0.1						-62.2	-35.5				-7.8
12.09.1999		10	8	47	4	W4M	171970	478.0	38.0	4.0	2.0	0.0	1535				-63.6	-46.8	-39.7	-32.5	-31.8	-28.3
30.08.2000	a1	1	9	52	4	W4M	4147	14.0	1.9	0.2	0.2						-43.6	-33.8	-32.4			-17.5
07.11.2003	c	8	14	52	4	W4M	319236	863.7	98.7	23.7	14.1	12.1			19.4		-63.0	-47.8	-39.1	-32.1	-33.0	-28.9
13.10.1999	16D	16	32	55	4	W4M	759954	1705.6	105.5	8.8	2.8	0.9					-65.9	-41.3	-33.6	-33.7		-50.6
30.07.2003	A	1	8	56	4	W4M	50273	176.2	15.7	3.9	1.3	25.7					-43.6	-42.9	-38.6	-30.9	-25.9	-35.3
08.06.2000		3	36	56	4	W4M	376245	1112.6	93.0	20.8	5.6						-62.9	-34.6	-37.3	-30.2	-34.5	-33.1

Appendix 2. Soil gases from the University of Alberta database - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

(cont.)

Date	UWI						C_1	C_2	C_3	C_4	C_5	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$^{13}C_{iC4}$	$^{13}C_{nC4}$	$^{13}C_{CO2}$
09.11.1999		3	36	56	4	W4M	731914	2239.9	199.8	21.2	13.4	5.0					-59.9	-44.4	-36.1	-29.0		-20.4
04.06.2004		7	26	11	5	W4M	779349	522.7	22.1	12.9	3.0	112.3					-83.0	-56.8	-39.6	-29.7	-34.4	
11.09.1999		7	11	47	5	W4M	54913	120.4	11.4	3.3	1.2	0.8					-61.2	-46.6	-40.6	-32.1		-64.2
17.07.2003	A	7	11	47	5	W4M	461080	1446.0	132.1	31.5	13.1	12.7					-63.4	-47.7	-39.7	-31.3		-66.5
02.11.2001		4	13	47	5	W4M	14837	52.4	7.7	1.9	1.3						-66.4	-43.9	-33.6	-32.1	-34.6	-39.5
29.10.2001		3	24	47	5	W4M	2843	12.4	4.8	6.7	6.8	33.0					-54.9	-39.7	-20.3	-25.8	-25.9	-24.6
25.08.2000	1c	1	36	47	5	W4M	189361	479.3	77.5	10.9	4.7						-70.3	-48.4	-38.3	-31.7	-35.5	-51.9
12.09.1999		10	17	48	5	W4M	255690	700.0	85.2	22.0	12.2						-64.1	-49.7	-41.4	-34.5	-36.7	-35.2
16.04.2000	6b	6	21	54	5	W4M	706815	1541.9	165.6	66.2	13.5						-63.4	-49.1	-39.5	-32.0	-37.0	-1.7
07.11.2001	c	10	7	55	5	W4M	34346	81.8	6.1	1.7	0.6	5.7			0.8		-58.5	-41.5	-41.5	-35.1	-29.0	-41.5
13.11.2000	a	11	7	55	5	W4M	332747	946.1	67.4	12.5	6.3	8.5			1.7		-60.6	-46.8	-40.0	-33.8	-30.3	-46.7
18.10.2001	d	8	7	55	5	W4M	204170	578.2	38.1	5.7	3.4						-64.3	-47.2	-42.2	-33.5	-29.5	-9.3
13.09.1999		12	7	55	5	W4M	48609	139.4	28.1	28.1	4.8	49.0					-61.2	-46.3	-40.0	-32.7	-29.5	-40.5
07.11.2001	c	13	7	55	5	W4M	177379	409.8	34.4	12.0	3.4				120.0		-60.2	-47.2	-38.9	-31.4		-39.7
13.11.2000	a	7	7	55	5	W4M	42330	96.9	7.3	3.8	1.6	29.0			2.3		-58.7	-47.1	-37.8	-31.2	-27.5	-35.4
18.10.2001	a	9	7	55	5	W4M	47537	92.4	6.7	1.6	0.8				0.2		-70.9	-52.4	-40.6	-30.6	-28.8	-56.3
07.11.2001	c	12	7	55	5	W4M	219284	1329.0	18.7	9.9	0.7	4.8					-56.9	-31.6	-23.9	-27.1	-26.5	-57.1
07.11.2001	c	11	7	55	5	W4M	794118	6111.5	232.1	61.4	18.1	17.0			2.0		-54.8	-29.9	-27.1	-26.3	-30.8	-22.8
13.11.2001		4	7	55	5	W4M	6942	66.6	7.0	8.3	3.5	141.0					-37.6	-22.7	-29.0			-26.7
26.11.2001	a	5	23	55	5	W4M	178716	401.2	42.0	23.6	16.1						-49.8	-46.7	-34.5	-22.7	-24.0	-34.8
21.11.2001	d	5	15	57	5	W4M	10735	22.9	1.2	0.5	0.1				1.6		-32.0	-24.9	-37.5	-26.2	-28.4	-31.2
14.05.2002	d	13	26	45	6	W4M	475	10.6	2.4	0.4	0.7	23.0			919.1		-65.4	-55.3	-33.6			-17.5
17.10.2001	d	6	30	45	6	W4M	123427	492.8	40.2	6.6	3.2	1.1					-72.0	-42.7	-38.0	-35.9	-30.7	-61.2
29.08.2000	6d	6	30	45	6	W4M	113987	235.3	23.7	11.5	2.4	4.0					-68.6	-50.5	-42.2		-34.1	-51.2
07.09.2000	b14	14	32	45	6	W4M	153899	897.8	293.2	137.6	35.7	5.5					-69.9	-37.4	-30.5	-29.3	-28.7	-4.0
07.09.2000	8c	8	3	46	6	W4M	405089	3922.8	1732.5	782.3	311.1	98.7					-54.5	-32.2	-28.1	-28.3	-28.8	-39.3
11.09.1999		11	29	46	6	W4M	723198	3334.7	490.1	82.8	45.8	14.5					-71.0	-44.9	-34.9	-31.1	-29.9	-38.6
07.09.2000	11c	11	29	46	6	W4M	718409	2924.1	496.3	238.4	55.8	15.3					-61.2	-40.2	-32.1	-29.5	-30.2	-35.5
15.08.2000		10	5	49	6	W4M	58632	0.1	0.2	0.2	0.1						-60.4					-39.4
10.05.2004		14	4	53	6	W4M	14508	30.0	4.5	2.9	0.5						-59.0	-32.3				-70.9
26.09.2000	a13	13	23	55	6	W4M	31677	76.6	8.8	4.4	1.7	367.0					-43.7	-45.1	-37.6	-32.2	-36.6	-20.8
08.06.2000		13	23	55	6	W4M	15216	85.6	19.3	16.4	3.9	707.0					-53.0	-42.4	-38.8	-31.6	-35.9	-31.4
26.09.2000	a14	14	23	55	6	W4M	4767	44.3	11.5	8.9	2.7	105.9					-36.8	-44.6	-37.8	-31.5	-33.2	-28.1
11.10.2000	1c	1	23	55	6	W4M	240265	1750.9	72.5	23.9	4.5						-52.8	-30.8	-30.5			-14.8
02.11.2000	13a	13	3	56	6	W4M	728907	2495.2	223.0	37.8	15.6						-61.4	-40.4	-32.8			-58.6
02.11.2000	12c	12	3	56	6	W4M	31363	82.7	6.4	0.9	0.5						-68.2	-42.9				-36.7
02.11.2000	13a	13	3	56	6	W4M	8457	22.9	2.2	0.3	0.2				523.3		-53.3					-26.3
06.08.2003		5	16	51	7	W4M	673234	594.5	215.8	55.2	21.9						-60.1	-45.9	-40.8	-32.8		-55.4
06.08.2003		5	16	51	7	W4M	202175	207.1	53.1	13.0	5.3	1.0			34.2		-67.5	-48.1	-38.5	-32.1		-42.0
22.08.2000	10d	10	13	52	7	W4M	22192	72.8	26.0	14.1	8.1	23.0					-50.7	-39.3	-36.4	-30.6	-33.8	-39.3
14.10.2001		10	22	52	7	W4M	598894	2121.0	198.4	57.1	19.3	22.6		0.0			-59.2	-44.4	-39.0	-31.2	-35.0	-46.3
17.06.2003		10	22	52	7	W4M	156384	379.4	32.2	10.8	2.8	4.1					-64.1	-43.1	-38.7	-31.0	-26.1	-43.5
27.09.2002	d	10	22	52	7	W4M	51897	154.0	12.5	3.9	1.2	18.0		0.3			-58.8	-27.3	-25.7			-32.6
19.11.1999		4	20	53	7	W4M	200180	493.8	44.8	8.8	3.6	2.5					-67.1	-48.0	-42.3	-34.8	-37.9	-35.2
27.04.1998	10d	10	36	62	7	W4M	37011	83.3	6.0	2.0	0.6						-68.6	-47.6	-40.2	-32.0		-53.2
10.05.2004		2	2	56	8	W4M	110423	84.9	8.1	8.7	0.6						-48.5	-40.4	-34.7	-28.4		-36.7
08.08.2004		7	35	57	12	W4M	73000	900.0					27000				-55.3	-29.3	-26.9	-25.3	-25.8	-50.1
29.06.2004		16	24	48	14	W4M	136258	57.9	5.0	1.1	0.5	4.4					-64.5	-53.0	-31.2			-10.9
24.06.1998		8	28	14	15	W4M	71400	0.0	0.0	0.0	0.0	0.0	13300				-38.8					-38.5
18.05.2000		6	34	55	15	W4M	448184	418.8	24.6	10.3	2.2						-66.7	-50.5	-50.6	-39.3	-30.5	-29.8
15.07.2004		10	7	14	16	W4M	363916	744.9	40.2	5.4	1.4						-64.2	-43.3	-31.0	-26.9	-25.7	-49.5
15.07.2005		7	14	14	16	W4M	856589	1464.0	96.7	14.3	4.2						-62.4	-45.8	-30.2	-26.6	-27.3	-51.0
20.04.1998		3	30	55	19	W4M	79357	73.9	2.5	1.1	0.1						-61.6	-45.8	-28.7	-29.6		-57.8
18.04.2004		6	19	23	21	W4M	254400	1000.0	100.0				13400				-42.9	-41.5				-22.6
23.07.2000		15	23	68	21	W4M	482877	992.5	58.0	15.8	6.7						-70.4	-49.8	-39.9	-32.4	-37.5	-42.8
23.07.2000		15	23	68	21	W4M	854987	1962.9	128.7	37.2	24.4	7.2					-67.6	-48.8	-39.7	-31.8	-34.1	-50.4
23.07.2000		15	23	68	21	W4M	789939	1775.7	117.3	33.5	24.4	7.1					-67.5	-48.2	-39.6	-31.7	-35.9	-55.3
15.07.2004		12	22	16	22	W4M	303750	862.0	65.9	13.1	7.3						-59.4	-39.4	-27.0	-26.4	-25.8	-53.5
20.07.2002		13	21	51	24	W4M	27094	48.9	6.0	2.7	1.1	15.4		1.6	2.9		-53.0	-49.4	-37.4	-30.1		-49.1

Appendix 3. Soil gas samples from the monitoring sites - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Well A3

Date	day	Location	C_1	C_2	C_3	C_4	C_5	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$
11.05.00		76.2m	147857	342	29	10.8	2.7		113				-66.6	-42.3	-37.0	-30.4	-30.1	-16.5
28.05.01									149				-64.8	-41.5	-36.6	-32.1		-17.7
17.05.00			151060	156	11	6.5	2.1		27098				-56.1	-38.2	-35.9	-29.3	-33.4	-77.3
28.05.01		?cm/110cm	319376	841	76	20.4	8.1						-55.7	-37.2	-34.2	-31.3	-34.2	-62.5
28.05.01		?cm/110cm	143381	319	34	9.9	3.6		85515				-52.1	-36.8	-33.2	-27.9	-30.7	-65.0
28.05.01		?cm/200cm	240048	573	50	12.7	5.1		113784				-58.5	-38.1	-35.9	-31.8		-66.2
28.05.01		30mSE/110cm	28	1	0	0.1	0.1		1148									-18.7
28.05.01		30mSE/200cm	21	0	0	0.0	0.1		2112									-30.3
11.07.01		5cm/70cm	634142	1702	144	35.4	15.1		19908				-57.7	-38.2	-34.6	-30.4	-33.9	-29.3
22.08.01		5cm/70cm	639010	1666	161	34.7	14.7		60202				-56.2	-35.6	-32.0	-30.3	-29.6	-57.4
22.08.01		1m/70cm	139603	391	41	12.53	4.8		126797				-51.9	-34.8	-32.8	-31.5	-31.8	-57.6
22.08.01		4m/50cm	32	0	0	0.0	0.1		1191									-40.3
2.11.01		30cm/70cm	83607	74	4	1.7	0.4		119759				-45.5	-35.3	-31.7	-30.1	-32.2	-68.0
2.11.01		1m/70cm	70490	94	8	2.5	0.8		128239				-45.5	-34.7	-31.6	-27.1	-27.7	-64.5
2.11.01		2m/70cm	1294	2	0	0.2	0.1		42082				-48.9					-63.8
2.11.01		3m/70cm	596	1	0	0.1	0.0		37673									-60.4
2.11.01		4m70cm	8	0	0		0.0		9107									-52.5
24.11.01		30cm/70cm	285753	322	20	6.7	1.7		352293				-51.9	-37.0	-34.1	-29.2	-33.4	-65.7
24.11.01		1m/70cm	99205	112	9	3.4	0.8		123565				-41.9	-34.9	-32.4	-29.7	-29.9	-66.3
24.11.01		2m/70cm	4835	6	0	0.2	0.1		46243									-65.7
24.11.01		3m/70cm	94	0	0	0.1	0.0		18746									-58.6
24.11.01		4m70cm	30	0	0	0.0	0.0		7951									-55.5
25.11.01		A1	253727	642	52	11.9	5.3		3465	173.7			-47.8	-37.1	-34.8	-27.1	-32.3	-22.9
25.11.01		A2	700	0	0	0.0	0.0		5337	36.1	1.4							-64.1
25.11.01		A3	20	2	0	0.3	0.1		95241	3.2								-53.0
25.11.01		B1	773244	1925	141	27.2	13.6		3338	549.8	14.1		-67.1	-41.6	-37.1	-29.3	-29.7	-28.0
25.11.01		B2	48818	135	11	3.1	1.4		103366	62.9	9.5		-51.4	-36.3	-36.9	-33.2	-31.4	-63.2
25.11.01		B3	154	0	0	0.0	0.1		18732	5.0			-45.2					-53.8
30.11.01		A1	341815	942	79	22.3	8.4		1827	188.1	1.5		-52.3	-35.6	-36.3	-31.9	-31.1	-30.5
30.11.01		A2	69	0	0	0.2	0.1		3347	34.7	1.7							-62.9
30.11.01		A3	410	2	0	0.1	0.1		38413	4.7	2.1							-51.8
30.11.01		B1	831679	2043	149	34.3	14.4		3144	610.1	4.6		-66.3	-40.8	-35.8	-30.8	-32.7	-26.8
30.11.01		B2	62942	197	18	5.7	2.1		120220	72.5	1.6		-48.8	-34.3	-32.7	-30.1	-29.4	-64.6
30.11.01		B3	24	0	0	0.0	0.1		18810	5.9	1.0							-55.9
14.12.01		A1	258198	554	40	14.8	3.6		21676	164.4	1.9		-51.8	-35.5	-32.9	-28.4		-66.2
14.12.01		A2	23	0	0	0.1	0.1		39916	33.4	1.3							-65.3
14.12.01		A3	33	0	0	0.0	0.1		5554		1.8							-52.8
14.12.01		B1	763927	1902	138	31.9	13.0		2100	612.0	2.7		-68.0	-41.3	-36.2	-30.1	-32.9	-28.8
14.12.01		B2	51249	168	16	4.9	1.8		113365	55.6	1.7		-48.8	-36.3	-30.6	-25.9		-65.4
14.12.01		B3	14	0	0	0.0	0.1		6426	8.2	1.4							-59.4
12.01.02	12	A1	341780	572	34	15.3	3.1		54704	187.1	1.8		-51.3	-35.4	-33.0	-28.4	-33.1	-77.1
12.01.02	12	A2	5095	2	0	0.1	0.0		44893	39.7	1.0		-35.0					-67.4
12.01.02	12	A3	59	0	0	0.0	0.0		6059	4.6								-63.2
12.01.02	12	B1	973575	2447	181	43.6	17.0		918	1168.2	0.9		-68.2	-41.9	-36.7	-31.9	-35.4	-37.1
12.01.02	12	B2	30932	93	11	4.2	1.3		154143	68.9	3.0		-45.1	-34.1	-30.4	-26.3	-29.3	-66.5
12.01.02	12	B3	42	0	0	0.0	0.0		5742	8.2								-61.2
26.01.02	26	A1	318924	435	23	10.1	1.6		69100	160.9	1.7		-50.5	-34.8	-32.2	-28.2	-32.0	-73.1
26.01.02	26	A2	7736	0	0	0.1	0.0		45327	33.8	1.4		-35.1					-69.6
26.01.02	26	A3	301	0	0	0.0	0.0		4552	4.2	0.9							-63.8
26.01.02	26	B1	870612	2208	159	36.4	14.7		726	984.6	1.3		-69.2	-43.1	-36.8	-30.6	-34.1	-35.1
26.01.02	26	B2	17361	45	6	2.3	0.7		155168	58.0	3.8		-44.9	-30.9	-31.6	-28.2	-32.6	-68.7
26.01.02	26	B3	18	0	0	0.0	0.0		8814	6.1								-62.7
09.03.02	68	A1	284225	553	31	11.8	1.8		60698	133.1	0.8		-46.6	-34.8	-32.0	-27.9	-30.5	-74.5
09.03.02	68	A2	35171	17	1	0.3	0.0		79914	38.6	0.9		-32.3					-67.4
09.03.02	68	A3	1582	0	0	0.2	0.0		15827	5.9	0.8		-39.2					-64.9
09.03.02	68	B1	989492	2151	183	36.8	18.7		402	1028.8	3.0		-68.7	-42.3	-36.7	-30.1		-34.2
09.03.02	68	B2	11074	5	1	0.3	0.1		168470	57.5	3.9		-42.1	-29.9				-69.8
09.03.02	68	B3	1765						11939				-35.1					-62.5
13.04.02	103	A1	287090	493	32	12.7	2.6		73200	161.7	1.5		-48.1	-35.0	-31.3	-27.1	-28.8	-74.9
13.04.02	103	A2	49246	2	0	0.0	0.0		76231	52.4	0.9		-37.9					-69.1
13.04.02	103	A3	3113	0	0	0.0	0.0		22685	12.3	1.3		-32.8					-64.0
13.04.02	103	B1	717463	1748	127	30.0	13.1		624	770.0	11.0		-68.2	-42.2	-36.9	-31.1	-34.6	-47.6
13.04.02	103	B2	60179	34	2	0.9	0.2		120869	75.0	1.8		-39.3	-34.1				-68.2
13.04.02	103	B3	171	0	0	0.0	0.0		7611	19.6	1.4		-37.8					-63.3
06.05.02	126	A1	154875	344	27	8.9	2.6		90480	92.0	4.9		-47.2	-34.7	-30.8	-27.1	-30.0	-71.4
06.05.02	126	A2	4097	0	0	0.4	0.0		140069	38.9	1.3		-33.9					-68.2
06.05.02	126	A3	179	0	0	0.2	0.0		66436	5.9	1.5							-63.5
06.05.02	126	B1	925964	2157	185	39.5	19.8		554	883.5	3.1		-68.9	-42.0	-37.1	-32.1	-33.2	-55.0
06.05.02	126	B2	19532	32	2	0.7	0.2		93631	23.2	2.6		-39.5	-28.2				-68.3

Appendix 3. Soil gas samples from the monitoring sites - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Well A3

Date	day	Location	C_1	C_2	C_3	C_4	C_5	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{C4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$
06.05.02	126	B3	6	0	0	0.2	0.1		17620	-4.0	2.3							-64.8
30.05.02	150	A1	226304	742	113	18.6	7.7		151642	117.0	18.6		-52.8	-37.7	-30.6	-27.7	-30.0	-67.8
30.05.02	150	A2	1981	4	1	0.9	0.2		6141	34.7	3.5		-45.6					-63.7
30.05.02	150	A3	99	0	0	0.2	0.4		30364	2.8	1.0							-61.3
30.05.02	150	B1	968668	2443	147	39.2	18.5		1475	881.2	3.9		-67.8	-41.9	-37.8	-32.2	-35.1	-63.3
30.05.02	150	B2	35039	106	10	3.0	1.3		193803	49.3	1.5		-46.3	-31.2	-30.1	-28.5	-29.6	-65.4
30.05.02	150	B3	37	0	0	0.2	0.2		28975	6.1	1.2							-61.4
18.06.02	169	A1	280644	903	142	18.9	8.5		106871	136.6	15.0		-52.8	-35.5	-31.9	-27.9	-30.3	-63.7
18.06.02	169	A2	12298	26	4	1.7	0.5		158707	45.6	4.5		-51.6	-34.1	-30.7	-27.3		-65.0
18.06.02	169	A3	7	0	0	0.3	0.0		15228	4.6	1.2							-59.8
18.06.02	169	B1	978148	2391	307	33.7	14.8		1329	992.9	2.9		-67.6	-42.1	-37.3	-31.6	-33.9	-53.4
18.06.02	169	B2	56475	159	17	4.0	1.5		141475	57.9	2.6		-53.7	-39.5	-31.7	-29.9		-64.0
18.06.02	169	B3	10	0	0	0.5	0.0		50647	7.8	0.9							-61.9
27.06.02	178	A1							36425				-53.6	-35.3	-33.3	-29.3	-31.7	-62.5
27.06.02	178	A2							138221				-52.1					-63.0
27.06.02	178	A3																-53.4
27.06.02	178	B1											-68.1	-41.8	-36.1	-31.8	-34.7	-48.6
27.06.02	178	B2							102907				-53.7	-38.7	-31.2	-26.7	-30.8	-62.3
27.06.02	178	B3																-58.6
27.06.02	178	C1											-62.9					-51.2
27.06.02	178	C2											-64.1					-52.5
27.06.02	178	C3											-62.6					-46.7
10.07.02	191	A1	280556	723	67	18.1	8.5		93365	134.3	15.7	11646	-52.8	-35.5	-33.6	-30.5	-32.7	-61.1
10.07.02	191	A2	18096	42	5	1.7	0.7		146211	41.3		22354	-50.8	-36.5	-34.4			-61.7
10.07.02	191	A3	20	0	0	0.0	0.0		15848	3.1								-56.9
10.07.02	191	B1	906388	1785	130	30.0	14.0		1056	1011.8	9.5		-67.8	-41.2	-36.7	-31.5	-34.9	-53.7
10.07.02	191	B2	59062	135	12	3.6	1.5		129829	58.5	4.0		-54.1	-38.8	-31.6	-27.2	-29.8	-60.5
10.07.02	191	B3	35	0	0	0.0	0.0		27185	6.5								-58.7
10.07.02	191	C1	8	0	<0.01	<0.01	0.0		3167	2.5	1.1							-51.9
10.07.02	191	C2	7	<0.01	<0.01	<0.01	<0.01		13993									-57.3
10.07.02	191	C3		<0.01	<0.01	<0.01	<0.01		1458									-49.0
21.07.02	202	A1	292036	734	68	17.9	8.4		86000	150.1	13.0	17874	-53.8	-35.9	-32.7	-28.5	-30.7	-62.0
21.07.02	202	A2	38758	85	10	3.2	1.3		157379	50.8	22.7	20147	-50.6	-34.6				-60.7
21.07.02	202	A3	21	0	0	<0.01	<0.01		13350	5.1								-60.4
21.07.02	202	B1	950160	1960	145	33.4	16.3		998	980.2	5.8	9647	-67.6	-41.7	-36.9	-31.8	-34.1	-59.5
21.07.02	202	B2	93191	209	19	5.0	2.3		149729	72.2	15.1	11556	-53.8	-35.4	-31.3	-30.0	-30.8	-61.1
21.07.02	202	B3	17	0	0	0.0	<0.01		22941	5.8								-59.7
21.07.02	202	C1	22	0	0	0.0	0.0		968	1.6								-50.9
21.07.02	202	C2	21	0	0	<0.01	<0.01		2054									-56.8
21.07.02	202	C3		0	0	<0.01	<0.01		1639									-51.4
08.09.02	251	A1	247897	784	83	20.1	10.5		111077	129.6	11.9	15682	-51.5	-35.1	-33.7	-29.9	30.1	-64.5
08.09.02	251	A2	21541	44	15	5.5	6.1		189253	55.6	8.4	16960	-50.0	-33.0	-30.2	-30.2		-62.5
08.09.02	251	A3	5	0	0	0.0	0.1		11104	5.7	2.4	193671						-56.8
08.09.02	251	B1	841737	2019	167	34.3	16.6		1199	903.0	13.0	8313	-66.9	-41.7	-36.8	-31.8	-35.1	-55.9
08.09.02	251	B2	53753	122	17	4.3	1.8		164567	687.1	13.9	29281	-52.5	-30.9	-32.8	-29.0	-31.0	-60.3
08.09.02	251	B3	789	2	0	0.1	0.0		8791	11.1	6.6	182556	-46.0					-58.1
08.09.02	251	C1	13	0	0	0.0	0.3		40406	157.0		193206	-55.3					-60.9
08.09.02	251	C2		0	0	0.1	0.0		7188			195090						-58.7
08.09.02	251	C3																
31.10.02	304	A1	211696	550	51	14.0	6.5		61679	124.2	3.1	20502	-49.3	-33.7	-32.6	-28.8		-67.1
31.10.02	304	A2	190	0	0	0.2	0.3		124892	44.1		35612	-33.1					-67.8
31.10.02	304	A3	14	0	<0.01	<0.01	<0.01		7814	3.6								-63.0
31.10.02	304	B1	868216	1732	129	29.4	14.4		698	939.2	8.2	12045	-67.6	-41.8	-36.7	-31.4		-50.2
31.10.02	304	B2	27740	83	8	2.5	0.9		47899	58.6	3.0	21209	-49.3	-44.4	-32.7	-28.7		-63.1
31.10.02	304	B3	5	0	<0.01	<0.01	<0.01		13451	7.3								-62.0
31.10.02	304	C1	1326	1	0	0.0	0.0		1111	4.0			-35.6					-64.1
31.10.02	304	C2	31	0	<0.01	<0.01	<0.01		5181	3.2								-65.1
31.10.02	304	C3	7	0	<0.01	<0.01	<0.01		1811	1.2								-58.7
24.11.02	328	A1	232384	681	70	18.0	9.4		109384	138.4	3.9	28377	-50.1	-36.1	-32.3	-26.1	-28.0	-68.2
24.11.02	328	A2	4443	54	10	4.1	4.5		149972	56.0	1.1	31615	-40.0					-68.0
24.11.02	328	A3	538	0	0	0.0	0.0		20506	10.0			-41.0					-66.8
24.11.02	328	B1	932874	1789	140	28.7	13.4		772	1021.1	10.1	9893	-69.1	-41.5	-37.1	-31.9	-35.7	-61.3
24.11.02	328	B2	65189	130	12	3.6	1.3		180876	79.7	4.7	11707	-50.1	-39.7	-32.3	-29.3	-31.3	-67.5
24.11.02	328	B3	7737	cant find					18129	15.1			-52.4	-30.2				-64.8
17.12.02	351	A1	222196	440	34	12.9	3.1		106195	123.1			-48.0	-36.7	-30.6	-26.9	-30.7	-70.1
17.12.02	351	A2	595	1	0	0.1	0.0		119142	47.3			-21.5					-66.6
17.12.02	351	A3	28	0	0	0.0	0.0		16087	6.2			-40.9					-64.0
17.12.02	351	B1	1012124	2240	180	37.4	18.3		277	1031.6	7.8		-68.2	-40.1	-36.7	-31.3	-34.4	-60.7
17.12.02	351	B2	42809	113	11	3.5	1.3		130005	68.2	1.6		-49.0	-30.8	-31.8	-28.3	-32.6	-67.4
17.12.02	351	B3	8	0	0	0.0	0.0		27093	11.9								-65.7

Appendix 3. Soil gas samples from the monitoring sites - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Well A3 (cont.)

Date	day	Location	C_1	C_2	$\dot{C}_2$	C_3	C_2	C_{4+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$
24.01.03	389	A1	224144	309	17	8.6	1.3		63749	111.0		76249	-45.7	-34.7	-34.5	-29.3	-33.6	-71.5
24.01.03	389	A2	13322	6	0	<0.01	0.0		63090	30.2			-40.2					-67.7
24.01.03	389	A3	505	0	0	<0.01	0.1		8043	5.2			-40.6					-63.4
24.01.03	389	B1	639214	1406	114	24.2	12.1		821	642.8	6.0	73888	-67.4	-42.0	-38.0	-32.8	-36.6	-50.4
24.01.03	389	B2	9842	0	0	<0.01	0.4		128489	53.6	2.0	61498	-45.5					-66.6
24.01.03	389	B3	83	0	0	<0.01	0.1		1314	7.2			-38.3					-64.1
04.03.03	425	A1	122921	157	8	12.9	5.8		47861	65.6			-44.5	-38.6	-30.9	-26.2	-29.8	-72.9
04.03.03	425	A2	19239	9	1	0.1	0.1		56631	30.1			-40.8					-69.7
04.03.03	425	A3	1089	1	0	0.0	0.0		6565	8.2			-43.8					-66.3
04.03.03	425	B1	803704	1768	142	33.1	16.7		1029	658.3	5.5	28975	-65.3	-41.3	-37.3	-32.2	-35.3	-69.0
04.03.03	425	B2	26874	48	5	<0.01	1.0		109043	51.3		24962	-42.3					-69.0
04.03.03	425	B3	234	0	0	0.1	0.1		18282	10.8								-63.8
27.03.03	451	A1	242304	533	49	12.9	5.8		63958	160.8	6.6	36074	-51.4	-36.8	-31.0	-26.3	-28.7	-72.0
27.03.03	451	A2	69625	4	0	0.1	0.1		69055	82.3	1.6	21499	-47.4					-71.7
27.03.03	451	A3	14793	6	1	0.0	0.0		15295	39.1			-46.8					-66.7
27.03.03	451	B1	749122	1776	151	33.1	16.7		2013	532.6	7.6	29577	-64.7	-41.2	-36.4	-30.2	-35.0	-73.0
27.03.03	451	B2	98449	121	9	<0.01	1.0		86186	108.5	3.6	29589	-51.5	-34.6	-31.4	-26.6	-28.2	-71.5
27.03.03	451	B3	9174	4	0	0.1	0.1		17371	38.7			-43.8					-67.1
01.05.03	486	A1	244932	737	75	<0.01	9.4		114997	115.0	3.6	34062	-50.6	-34.8	-33.8	-29.6	-33.2	-68.5
01.05.03	486	A2	15847	43	5	<0.01	0.6		144757	47.2	1.8	29322	-47.5	-28.2	-26.1			-66.0
01.05.03	486	A3	18	0	0	0.0	<0.01		10536	6.7								-63.7
01.05.03	486	B1	775436	1789	148	32.1	16.3		4214	597.5	6.0	28430	-64.7	-41.4	-37.1	-34.5	-36.9	-70.8
01.05.03	486	B2	95911	261	25	<0.01	2.8		117429	78.2	13.8	35986	-51.3	-34.9	-31.8	-26.3	-32.5	-68.2
01.05.03	486	B3	27	0	0	0.1	0.0		18250	16.5	2.6	193247	-58.9					-66.4
19.06.03	535	A1	307530	887	89	nd	10.9		97079	153.8	7.9	4982	-51.8	-38.1	-32.4	-29.2	-32.3	-64.6
19.06.03	535	A2	37626	81	9	nd	1.1		168243	49.1	16.0	6269	-51.5	-32.3	-29.7	-28.9	-29.2	-64.4
19.06.03	535	A3	15	0	0	0.0	0.0		26806	5.9								-63.0
19.06.03	535	B1	853858	2010	169	36.6	18.5		270	724.4	6.2	2668	-67.2	-42.3	-37.0	-31.0	-37.4	-64.7
19.06.03	535	B2	77669	206	20	nd	2.2		174934	65.3	27.0	5337	-53.0	-34.8	-32.2	-29.8	-31.7	-65.5
19.06.03	535	B3	12	0	0	0.1	0.0		59601	11.5		155874						-63.7
19.06.03	535	C1	15						527									-52.9
19.06.03	535	C2	13						4167	-5.8	0.7							-53.3
19.06.03	535	C3	12						2971	-7.2								-41.6
05.08.03	582	A1	139023	487	46	12.3	6.1		68726	135.2	11.4	15232	-51.7	-34.8	-31.5	-27.4	-30.6	-60.8
05.08.03	582	A2	137	0	1	0.4	0.1		32740	39.3	1.5	55275	-51.0					-62.1
05.08.03	582	A3	4						23411	4.9	0.2	176123						-57.7
05.08.03	582	B1	789314	1023	86	19.2	9.7		5902	722.7	30.6	15796	-63.8	-41.6	-36.2	-31.1	-34.3	-65.2
05.08.03	582	B2	42405	151	13	3.6	1.6		73255	72.3		27238	-53.1	-33.6	-31.4	-26.2	-29.5	-61.6
05.08.03	582	B3	245	1	0	0.1	nd		45691	10.0	1.3	204749		-33.4	-31.3	-27.1	-30.0	-59.7
05.08.03	582	C1	36	0	0	0.0	0.1		11196	3.2	0.2	211689						-60.1
05.08.03	582	C2	14	0	0	0.0	0.0		5488	1.9		184714						-56.6
05.08.03	583	C3		2	r	r	0.1		3211			169625						-48.9
28.08.03	605	A1	212476	637	72	19.3	10.2		142767	120.2	7.6	13531	-50.8	-34.6	-32.2	-29.2	-31.1	-61.7
28.08.03	605	A2	181	0	0	0.2	0.1		38644	48.9		41544	-44.0					-62.1
28.08.03	605	A3	360	0	0	0.0	0.2		23101	3.2	0.9	218808	-40.0					-56.0
28.08.03	605	B1	808972	2038	175	34.7	18.3		5707	762.6	29.4	16667	-63.7	-41.1	-35.5	-29.2	-32.4	-63.7
28.08.03	605	B2	55321	143	17	4.7	2.1		153294	269.6	40.2	17970	-52.2	-33.5	-30.0	-26.1	-29.3	-61.7
28.08.03	605	B3	261	1	0	0.1	0.2		19966	8.2		185496						-58.0
28.08.03	606	C1	28	0	0	0.1	0.2			7.7	1.1		-60.5					-63.1
28.08.03	607	C2	172	0	0	0.0	0.0		8358	3.4	3.5	219475						-59.2
28.08.03	608	C3		0	0	0.1	0.2		7328			217302						-51.4
12.09.03	620	A1	215012	639	73	19.2	11.1		34167	119.6	10.1	16642	-58.7	-39.4	-33.9	-28.9	-32.4	-63.1
12.09.03	620	A2	18530	60	13	5.1	6.2		37324	45.2	7.4	16255	-49.0					-61.0
12.09.03	620	A3	6	0	0	0.1	0.0		21890		0.7	211719						-59.5
12.09.03	620	B1	880758	2102	173	35.2	16.9		1642	1196.8		20321	-68.2	-41.6	-37.4	-32.4	-36.8	-68.0
12.09.03	620	B2	53560	137	18	4.2	1.8		60891	691.6	16.5		-54.1	-39.2	-32.6	-29.1	-32.3	-62.0
12.09.03	620	B3	647	2	1	0.1	0.0		49517	0.3	1.2	186029	-51.9					-62.7
12.09.03	621	C1	51	0	0	0.1	0.0					211689						
12.09.03	622	C2	11	0	0	0.0	0.0			2.6	4.4							
12.09.03	623	C3																
18.09.03	626	A1							56529				-59.7	-38.3	-34.8	-30.2	-34.6	-65.3
18.09.03	626	A2							123856				-51.0	-35.1	-34.3			-65.0
18.09.03	626	A3		0					32583		0.7	219877						-61.3
18.09.03	626	B1		1895	170	38.9	19.8		313			8432	-67.4	-41.3	-37.3	-30.9	-35.9	-66.4
18.09.03	626	B2							211466		1.2		-53.7	-35.5	-33.5	-29.6	-32.9	-63.1
18.09.03	627	B3		0					46199			349018		-34.5	-31.4	-29.5	-1.5	-62.0

Appendix 3. Soil gas samples from the monitoring sites - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Well A3 (cont.)

Date	day	Location	C_1	C_2	C_3	iC_4	nC_4	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$
										378.1								
27.09.03	635	A1	547114	1534	142	31.4	14.9		62538	377.0	6.0		-59.1	-37.9	-36.0	-30.2	-33.7	-61.6
27.09.03	635	A2	51012	122	16	4.9	2.0		141757	73.2	3.4	16036	-51.1	-35.5				-65.1
27.09.03	635	A3	4	0	0	0.0	0.0		25106	8.6	0.7	188176						-62.6
27.09.03	635	B1	804367	1940	163	34.0	15.6			792.1	31.0	13362	-64.7	-40.6	-36.0	-31.1	-34.2	-64.2
27.09.03	635	B2	118940	283	32	7.7	3.2		134425	116.2	16.9	13028	-53.7	-35.4	-32.7	-29.6	-33.0	-62.7
27.09.03	635	B3	1	0	0	0.0	0.0		37676	23.5	7.0	199256						-62.5
27.09.03	635	C1	101	0	0	0.0	0.0		1163	1.1	5.0							-39.7
27.09.03	635	C2		1	1				2327		1.6							-56.8
27.08.03	635	C3							545		0.9							-37.7
02.10.03	640	A1	487794							321.9		27533	-58.7	-37.7	-35.5	-30.5	-35.0	-64.2
02.10.03	640	A2	47927							84.5	4.4	13674	-51.9	-35.2	-32.5	-29.2	-32.0	-64.6
02.10.03	640	A3	2							16.2	2.9	188672						-63.3
02.10.03	640	B1	762124							680.5	30.5	8207	-62.8	-40.9	-35.8	-31.3	-35.0	-62.0
02.10.03	640	B2	118885							109.9	4.0	12818	-52.8	-34.7	-33.4	-29.3	-34.3	-64.8
02.10.03	640	B3	20							16.6	2.8	180881						-62.6
02.10.03	640	C1										198858						-53.5
02.10.03	640	C2																-61.0
02.10.03	640	C3																-53.6
16.10.03	654	A1	525868							435.4	3.4	13202	-57.5	-37.4	-34.5	-28.8	-34.5	-64.6
16.10.03	654	A2	44724							75.7	5.5	24275	-49.4	-34.0	-31.9	-28.7	-1.5	-65.2
16.10.03	654	A3	25							63.3	3.8	117846	-43.5					-63.6
16.10.03	654	B1	620421							895.1	28.0	13809	-59.5	-39.2	-35.8	-34.4	-34.9	-61.3
16.10.03	654	B2	122282							103.6	14.8	17922	-53.4	-34.5	-32.8	-28.8	-33.0	-65.3
16.10.03	654	B3	25							63.3	3.7	181247						-63.7
16.10.03		C1	437															-50.3
16.10.03		C2																-57.1
16.10.03		C3																-50.3
25.10.03	663	A1	462298	1303	124	27.6	13.3		68077	542.4	4.7	8262	-56.6	-37.[illegible]	-34.4	-29.6	-32.9	-65.7
25.10.03	663	A2	42832	67	13	3.7	1.2		165209	79.5	2.9	1170	-49.2	-34.0	-33.8	-29.3		-67.5
25.10.03	663	A3	3	0	0	0.0	0.0		19808	17.6	0.5	195737						-63.9
25.10.03	663	B1	572587	1623	150	33.0	16.0		1115	1012.2	13.4	5765	-58.2	-38.5	-35.4	-30.8	-34.5	-54.0
25.10.03	663	B2	131457	348	39	9.6	4.1		158844	112.2	10.0	771	-52.5	-35.1	-33.0	-29.3	-32.3	-66.4
25.10.03	663	B3	3	0	0	0.0	0.0		35140	120.4	3.0	186753						-64.2
25.10.03	663	C1	1071	0	0	0.0	0.0		5441	33.0	2.7	204888	-33.8					-63.4
25.10.03		C2							2115									-56.3
25.10.03		C3							1782									-47.4
08.11.03	677	A1	425240	1167	112	25.8	12.0		63403	263.2	3.7	5240	-56.4	-37.3	-34.3	-29.9	-33.4	-66.7
08.11.03	677	A2	20725	18	4	1.5	0.3		159407	259.5	3.0	20843	-43.1	-1.5	-30.8			-68.9
08.11.03	677	A3	60	1	0	0.0	0.0		13515	35.0	2.6	192115						-65.5
08.11.03	677	B1	758494	2029	178	37.6	18.4		?	609.4	13.8	9316	-62.2	-39.6	-36.1	-31.4	-34.1	
08.11.03	677	B2	80530	167	22	5.8	2.3		111806	593.6	7.1	12145	-50.2	-34.5	-32.5	-28.5	-31.5	-66.9
08.11.03	677	B3	10	0	0	0.0	0.0		15753	17.2	1.0	177401						-65.3
26.11.03	695	A1	388961	1021	103	25.1	11.4		76188	228.4	2.6	18027	-53.8	-35.3	-34.1	-29.9	-34.1	-68.0
26.11.03	695	A2	8245	4	1	0.2	0.0		108510	56.3	2.8	46431	-39.6					-69.8
26.11.03	695	A3	2	0	0	0.0	0.0		17016	9.9	2.0	192115						-65.5
26.11.03	695	B1	899457	2209	187	38.3	18.9		21349	981.4	13.7	318	-67.1	-41.6	-36.6	-31.0	-34.1	-62.5
26.11.03	695	B2	91340	201	23	6.3	2.6		141147	96.2	5.8	12464	-49.5	-33.5	-32.8	-27.9	-31.8	-68.7
26.11.03		B3	25	0	0	0.0	0.0		25841	8.3	4.0	193129						-65.4
23.12.03	722	A1											-50.8	-35.5	-33.1	-29.0	-32.2	-71.2
23.12.03	723	A2											-30.3					-69.1
23.12.03	724	A3							31725									-65.7
23.12.03	725	B1	966956										-68.2	-42.0	-36.5	-31.1	-34.6	-62.1
23.12.03	726	B2											-47.8	-33.5	-31.4	-22.3		-68.7
23.12.03	727	B3							42915									-65.7
07.02.04	768	A1	221122						45298				-49.4	-34.9	-32.8	-28.9	-34.2	-73.5
07.02.04	768	A2	12566						53396				-40.1					-69.4
07.02.04	768	A3							11888									-64.6
07.02.04	768	B1	943749										-68.1	-42.0	-36.6	-30.6	-34.9	-55.7
07.02.04	768	B2	14551						109087				-47.3	-33.8	-34.9			-67.1
07.02.04	768	B3							18896									-64.6
07.02.04	768	C1							554				-47.1					-65.0
16.04.04	867	A1	277186						44243				-55.7	-37.2	-33.7	-29.6	-34.4	-71.0
16.04.04	867	A2	56061						92518				-44.8	-32.9	-31.0	-26.4	-1.5	-71.0
16.04.04	867	A3																
16.04.04	867	B1	######										-66.2	-40.9	-34.7	-30.5	-34.5	-59.7
16.04.04	867	B2	99314						115479				-49.1	-34.1	-32.1	-27.9	-31.4	-69.4
16.04.04	867	B3							33818									-67.0
16.04.04	867	C1	8461						3559				-38.5					-58.0

Appendix 3. Soil gas samples from the monitoring sites - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Well A3 (cont.)

Date	. day	Location	C_1	C_2	C_3	C_4	C_4	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$
07.07.04	950	A1	688405						56467				-60.7	-37.9	-35.5	-30.6	-33.1	-61.5
07.07.04	950	A2	179206						133071				-55.3	-35.2	-32.8	-30.4	-32.4	-58.4
07.07.04	950	A3							32019									-57.8
07.07.04	950	B1	874995						11976				-69.6	-41.4	-36.3	-31.5	-34.4	-62.6
07.07.04	950	B2																
07.07.04	950	B3							57615									-62.1
27.08.04	1002	A1	576789	1342	124	27.9	13.6		44556	425.3			-60.3	-39.8	-35.2	-30.8	-34.2	-57.7
27.08.04	1002	A2	130090	316	36	9.1	4.3		122793	105.5			-53.8	-35.0	-32.9	-29.4	-33.1	-59.1
27.08.04	1002	A3	10	0	0	0.0	0.1		29413	7.8								-57.7
27.08.04	1002	B1	778590	1560	136	28.2	14.8		16671	979.2			-68.0	-41.6	-36.4	-31.0	-33.9	-66.5
27.08.04	1002	B2	195772	501	53	12.8	6.2		127663	132.3			-54.1	-35.7	-32.8	-30.5	-35.3	-57.9
27.08.04	1002	B3	17033						88486	-6.0			-44.5	-34.7	-31.1	-30.0		-63.0

Appendix 3. Soil gas samples from the monitoring sites - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Well A4

Date	. day	Location	C_1	C_2	C_3	C_4	C_4	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$
08.09.02													-61.0	-43.2	-33.5	-31.6	-33.6	-27.5
17.05.00		110cm	92098	78	5	7.1	1.4		91403				-54.8	-38.1	-34.7			-79.3
11.07.01		10cm/70cm	375367	939	99	31.9	9.0		12438				-56.7	-41.6	-37.8	-32.2	-36.0	-67.0
22.08.01		5cm/70cm	212655	411	40	14.2	3.5		96985				-61.7	-41.6	-36.9	-28.9	-35.9	-66.5
22.08.01		1m/70cm	688	2	0	0.2	0.1		83064				-62.3					-59.1
22.08.01		5m/70cm	9	0	0	0.0	0.1		334									-27.1
02.11.01		40cm/70cm	106407	161	23	8.5	2.1		70648				-60.7	-40.9				-72.9
02.11.01		1m/70cm	74	0	0	0.1	0.0		23214				-57.4					-57.7
02.11.01		2m/70cm	13	0	0	0.0	0.0		9367									-43.9
02.11.01		3m/70cm	18	0	0	0.0	0.0		3645									-36.7
02.11.01		4m/70cm	5	0	0	0.0	0.0		4418									-26.8
30.11.01		40cm/70cm											-54.6	-41.9	-37.3	29.0		-75.8
06.05.02		40cm/70cm	462063	662	45	16.1	2.6		27040				-61.7	-42.4	-37.5	-31.9		-75.8
06.05.02		1m/70cm	7739	1	0	0.2	0.2		3100				-58.8					-68.9
06.05.02		2m/70cm	99	0	0	0.3	0.3		1036				-34.3					-64.5
06.05.02		3m/70cm	19	0	0	0.0	0.0		4205									-40.5
18.06.02	169	A11	67620	227	46	9.9	2.4		114232	103.2	9.0		-53.3	-40.8	-37.3	-31.7		-67.2
18.06.02	169	A12	5	0	0	0.7	0.0		22070	21.3	1.0							-59.4
18.06.02	169	A13	5	0	0	0.5	0.0		5256	14.2	1.6							-36.9
18.06.02	169	A14	8	0	0	0.5	0.1		2814	12.6	1.1							-24.7
18.06.02	169	B11	57921	148	16	3.9	1.1		31782	122.3	9.3		-66.6	-43.9	-37.8	-30.2		-52.0
18.06.02	169	B12	134	1	0	0.4	0.1		5976	0.2	3.0		-39.2					-32.1
18.06.02	169	B13	6	0	0	0.6	0.1		2724	11.5	6.0							-18.9
18.06.02	169	B14	8	0	0	0.4	0.0		1593	13.4	4.1							-16.5
27.06.02	178	A11											-53.0	-41.6	-31.8	-28.6		-67.4
27.06.02	178	A12							24374				-50.1					-56.9
27.06.02	178	A13							6863									-36.4
27.06.02	178	A14							2988									-21.8
27.06.03	178	B11											-53.8	-39.5	-36.1	-1.5		-61.4
27.06.02	178	B12																-46.2
27.06.02	178	B13							1595				-46.2					-19.4
27.06.02	178	B14																
27.06.02	178	C11																-37.3
27.06.02	178	C12																-27.2
27.06.02	178	C13																-21.8
10.07.02	191	A11	267048	827	87	28.7	8.9			187.5	4.5	9590						
10.07.02	191	A12	80	0	0	<0.01	0.0		25441									-59.9
10.07.02	191	A13	13	0	0	<0.01	0.0		4837	17.1								-42.1
10.07.02	191	A14	6	0	0	<0.01	0.0		3468		1.3							-19.4
10.07.02	191	B11	704726	1729	152	43.8	####		773	987.4	283.6	10259	-67.7	-46.1	-39.9	-31.3	-32.5	-35.0
10.07.02	191	B12	217	1	0	0.0	0.1		19788	19.3	17.1							-53.4
10.07.02	191	B13	3	0	0	0.0	0.2		11219	nd	8.0							-35.9
10.07.02	191	B14	8	0	0	0.0	0.0		4134	nd	4.5							-29.9
10.07.02	191	C11	37	0	0	0.0	0.0		3312	nd	1.1							-32.0
10.07.02	191	C12	11	0	0	<0.01	0.0		2201	nd								-18.9
10.07.02	191	C13	6	<0.01	<0.01	<0.01	<0.01		2140	nd								-16.0

Appendix 3. Soil gas samples from the monitoring sites - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Well A4

Date	day	Location	C_1	C_2	C_2	C_2	C_2	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$	$\delta^{13}C_{CO2}$
21.07.02	202	A11	369060	1123	116	34.0	11.6		45875	240.6	5.7	12932	-54.5	-40.8	-37.7	-32.3	-34.9	-68.2
21.07.02	202	A12	8	0	0	0.0	0.0		21916	1216.3								-57.8
21.07.02	202	A13	6	<0.01	<0.01	<0.01	0.0		6346	nd								-39.8
21.07.02	202	A14	5	<0.01	<0.01	<0.01	<0.01		3170	nd								-28.0
21.07.02	202	B11	691[illegible]	1703	149	43.0	13.9		nd	985.5	271.4	13690	-67.6	-45.6	-39.8	-33.3	-34.9	
21.07.02	202	B12	13	0	0	0.0	0.0		25094	21.3	19.8							-55.9
21.07.02	202	B13	2	<0.01	0	0.0	<0.01		7028	nd	11.5							-36.2
21.07.02	202	B14	6	<0.01	<0.01	<0.01	0.0		3847	nd	3.7							-30.0
21.07.02	202	C11	46	0	0	0.1	0.0		1039	nd								-55.5
21.07.02	202	C12	12	0	0	<0.01	<0.01		928	nd			-47.5					-41.8
21.07.02	202	C13	6	<0.01	<0.01	<0.01	<0.01		733	nd								-28.7
08.09.02	251	A11	589787	1616	161	44.4	14.0		34696	334.0	10.0	22308	-59.0	-42.4	-38.2	-32.0	-35.4	-51.6
08.09.02	251	A12	3	0	0	0.0	0.0		42004	10.9	4.0	177441						-52.4
08.09.02	251	A13	3	1					6764	8.4	3.0	208019						-37.5
08.09.02	251	A14	2	0	0	0.6	0.1		4821	6.1	5.1	188032						-23.6
08.09.02	251	B11	809001	1794	176	44.5	14.4			931.0	228.0	28327	-69.4	-45.6	-39.7	-33.0	-1.5	-47.3
08.09.02	251	B12	4	0	0	0.0	0.0		31162	19.0	3.7	162443						-46.3
08.09.02	251	B13	3	0	0	0.0	0.0		9125	16.3	6.2	211902						-33.6
08.09.02	251	B14	2	0	0	0.1	0.0		6218	7.0	3.6	187737						-24.2
08.09.02	251	C11	45	1	0	0.0	0.0		8142	9.5	6.3	199275	-67.7					-56.9
08.09.02	251	C12							1024									-41.0
08.09.02	251	C13	4	0	0	0.0	0.0		1020		4.8	190201						-27.3
08.09.02	251	C14							1234				-41.9					-23.2
31.10.02	304	A11	405569	1138	111	34.4	11.0		25322	301.7	4.0	10000	-59.9	-42.2	-37.5	-29.7	-1.5	-70.3
31.10.02	304	A12	23	0	0	0.0	0.0		23099	18.7			-42.7					-59.6
31.10.02	304	A13	5	0	<0.01	<0.01	<0.01		4563	ND								-42.9
31.10.02	304	A14	29	0	0	0.0	0.0		2313	ND								-26.6
31.10.02	304	B11	642530	1562	139	40.1	13.1			6.7	234.2	13132	-69.2	-45.5	-39.6	-33.1	-1.5	-72.9
31.10.02	304	B12	31	0	0	0.0	0.0		19756	18.9	3.1		-56.5					-49.2
31.10.02	304	B13	6	0	0	0.1	0.0		7998	6.3								-40.7
31.10.02	304	B14	4	0	<0.01	<0.01	0.0		3109	ND								-25.5
31.10.02	304	C11	245	0	0	0.0	0.0		2815	6.9			-63.9					-58.6
31.10.02	304	C12	10	0	0	0.0	<0.01		1704	ND								-48.8
31.10.02	304	C13	3	0	<0.01	<0.01	<0.01		1214	ND								-37.6
31.10.02	304	C14	7	0	<0.01	0.0	<0.01		613	12.5								-14.8
24.11.02	328	A11																
24.11.02	328	A12	49	1	0	0.0	0.0		5174	13.8		10005	-50.2					-61.8
24.11.02	328	A13	11	n.d.	n.d.	n.d.	n.d.		3057	18.6	0.4	195235	-61.1					-49.3
24.11.02	328	A14							1959				-62.6					-24.8
24.11.02	328	B11	871900	1965		51.6	16.9		391	1106.0	268.9		-68.9	-45.6	-40.0	-34.1	-35.6	-33.6
24.11.02	328	B12	23	0	0	0.2	0.3		17310	13.1	1.8	18880	-56.9					-49.8
24.11.02	328	B13	1	0	n.d.	n.d.	n.d.		37865	17.4	2.5	228112	-61.3					-43.3
24.11.02	328	B14	1	0	n.d.	n.d.	n.d.		250	108.3	0.8	208936	-66.2					-26.6
												203702						
17.12.02	351	A11	739645	1550	152	45.8	13.3		40414	441.8	4.5	13699	-59.7	-42.1	-36.8	-30.7	-33.6	-79.7
17.12.02	351	A12	8229	0	0	0.0	0.0		15687	25.8	0.9		-39.0					-62.2
17.12.02	351	A13	1440	0	0	0.0	0.0		5166	17.0	2.3		-36.1					-51.7
17.12.02	351	A14	40	0	0	0.0	0.0		1023	0.0			-46.9					-27.0
17.12.02	351	B11	998611	2115	205	55.1	18.5		126	1124.1	267.6	12510	-69.3	-45.6	-40.1	-33.5	-37.2	-41.5
17.12.02	351	B12	2778	1	0	0.1	0.0		14494	24.3	4.1		-37.2					-52.5
17.12.02	351	B13	1094	0	0	0.0	0.0		5409	15.6	3.7		-35.0					-47.2
17.12.02	351	B14									2.8							
24.01.03	389	A11	629123	1396	127	38.1	8.7		18165	333.0	1.8	48402	-58.8	-42.0	-37.8	-32.6	-35.7	-76.6
24.01.03	389	A12	17784	8	1	<0.01	0.0		9245	24.6			-47.2					-62.3
24.01.03	389	A13	2843	1	0	<0.01	0.1		3098	7.9			-44.8					-47.3
24.01.03	389	A14	188	0	0	<0.01	0.0		1513	nd			-42.6					-28.6
24.01.03	389	B11	870263	1791	172	46.0	15.3		182	893.6	244.4	40922	-69.3	-45.5	-40.5	-34.5	-37.9	-34.9
24.01.03	389	B12	12772	6	0	<0.01	0.1		10697	21.7			-44.2					-57.1
24.01.03	389	B13	3168	<0.01	0	<0.01	0.0		6442	15.6			-42.0					-44.2
24.01.03	389	B14	47	0	<0.01	0.0	0.0		523	nd			-33.9					-30.0
04.03.03	425	A11	119725	126	3	<0.01	0.1		33714	64.6		209577	-50.8					-70.8
04.03.03	425	A12	21789	11	1	<0.01	0.0		472	22.5							########	-10.29
04.03.03	425	A13	3529	2	0	<0.01	0.0			7.0			-41.7					-46.0
04.03.03	425	A14	283	0	<0.01	0.0	0.0			13.7								
04.03.03	425	B11	809456	1600	148	38.4	12.0			938.8	254.8	18103	-69.6					
04.03.03	425	B12	54820	18	2	<0.01	0.1		13447	33.5			-45.7					-57.7
04.03.03	425	B13	6280	3	2	<0.01	1.3		7236	19.6			-44.9					-40.0
04.03.03	425	B14	279	0	<0.01	0.0	0.0		3600	7.1			-43.7					-30.3

Appendix 3. Soil gas samples from the monitoring sites - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Well A4

Date	day	Location	C_1	C_2	C_3	C_2	C_2	C_{4+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{C4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$
27.03.03	451	A11	244249	152	2	1.4	0.0		50188	128.5	3.9	47360	-53.4	-42.4			–	-71.0
27.03.03	451	A12	38585	10	0	0.2	0.0		10796	31.0	6.4		-40.9					-52.1
27.03.03	451	A13	10637	6	0	0.0	0.0		3089	16.4			-37.9					-50.0
27.03.03	451	A14	1806	1	0	<0.01	0.0		1355	nd	2.4		-39.0					-28.9
27.03.03	451	B11	686782	1412	139	38.2	12.7		209	728.7	196.5		-68.7	-46.5	-40.7	-34.0	-37.3	-55.4
27.03.03	451	B12	91878	100	7	3.6	0.3		44974	65.7	1.2	56736	-46.7					-40.5
27.03.03	451	B13	10897	10	1	0.2	0.1		15475	21.4		205554	-43.1					-30.7
27.03.03	451	B14	2683	2	0	0.0	0.0		4024	10.0			-40.3					-29.5
01.05.03	486	A11	625792	1395	146	43.0	14.0		32509	379.7	2.1	32493	-62.4	-43.7	-38.4	-32.0	-34.8	-77.2
01.05.03	486	A12	8849	4	0	0.1	0.1		18366	24.0			-42.7					-64.9
01.05.03	486	A13	40	0	0	<0.01	0.0		11781	6.2								-51.6
01.05.03	486	A14	16	0	<0.01	<0.01	0.0		8116	11.6								-30.6
01.05.03	486	B11	810321	1682	165	45.9	15.4		623	837.5	225.4	28007	-71.1	-46.0	-40.2	-33.1	-36.1	-46.0
01.05.03	486	B12	[illegible]	6	0	0.3	0.1		22026	31.4	1.4		-40.3					-63.4
01.05.03	486	B13	[illegible]	0	0	0.2	0.3		15678	16.6								-39.5
01.05.03	486	B14	12	0	0	0.0	0.0		9910	6.3								-32.7
19.06.03	535	A11	677352	1601	169	nd	16.2		35063	424.8	4.9	4473	-62.9	-45.0	-38.2	-32.0	-35.3	-73.4
19.06.03	535	A12	160	0	0	0.0	0.0		38693	19.8								-64.0
19.06.03	535	A13	29	0	0	0.0	0.0		7695									-41.8
19.06.03	535	A14																
19.06.03	535	B11									219.8	4357	-70.0	-46.2	-39.9	-33.6	-37.0	-50.4
19.06.03	535	B12	114	0	0	0.0	0.0		80125	21.7								-59.2
19.06.03	535	B13	27	1	0	0.4	0.2		7268	5.5	1.1							-39.0
19.06.03	535	B14	17	0	0	0.0	nd		6809									-27.8
19.06.03	535	C11							4701									-52.4
19.06.03	535	C12							3530									-42.6
19.06.03	535	C13							1615									-29.5
19.06.03	535	C14																
09.08.03	582	A11	679842						47625		16.1	20719	-61.4	-45.6	-40.4	-34.0	-37.5	-69.1
09.08.03	582	A12	12	0	0				33216	11.2	1.0	154239						-54.8
09.08.03	582	A13	26	0					9481	5.8	0.2	186570						-37.0
09.08.03	582	A14	10	0					6903	5.3	0.8	194722						-22.2
09.08.03	582	B11		947	93	26.4	8.9			r	297.8	26189	-68.3	-45.2	-41.2	-35.0	-39.0	-68.1
09.08.03	582	B12	131	1	0	0.0	0.0		60961	11.0	2.0	292800						-51.3
09.08.03	582	B13	12	0					18627	4.9	0.2	163100						-32.6
09.08.03	582	B14	54	0	0	0.0	0.0		9816	5.3	1.7	193200						-23.1
09.08.03	582	C11	35	0	0	0.0	0.0		1968	6.5	0.2	193600	-48.8					-48.9
09.08.03	582	C12	13	0	0	0.0	0.0		1144	4.9	0.9	203400						-34.7
09.08.03	582	C13	7	0	0	0.0	0.0		887	5.3	0.2	195200						-22.0
09.08.03	582	C14	9	0	0	0.0	0.0		730	5.0	0.1	196300						-12.9
28.08.03	605	A11	661300	1510	176	52.4	18.8		30600	387.8	10.5	15163	-60.8	-42.1	-39.5	-32.6	-36.8	-62.3
28.08.03	605	A12	13	0	0	0.0	0.0		26332	17.8		163574						-52.9
28.08.03	605	A13	23	0	0	0.0	0.0		1154	39.9		atm						-38.4
28.08.03	605	A14	37	0	0	0.0	0.0		784	19.2	7.8	203169						-16.1
28.08.03	605	B11											-68.4	-46.4	-38.9	-32.8	-39.0	-55.4
28.08.03	605	B12	4	0	0	0.0	0.0		39719	59.4		16516						-48.6
28.08.03	605	B13	16	0	0	0.0	0.0		14161	8.0	1.1	207000						-35.0
28.08.03	605	B14	10	0	0	0.0	0.0		8000	0.0		39988						-24.5
28.08.03	605	C11	82	0	0	0.0	0.0		2913	13.6		202970						-52.0
28.08.03	605	C12	5	0	0	0.0	0.0		1425	6.1	1.1	28922						-37.1
28.08.03	605	C13	10	0	0	0.0	0.0		995	5.9		202931						-26.8
28.08.03	605	C14	29	0	0	0.0	0.0		461	0.0		28372						-21.0
12.09.03	620	A11	590287	1349	158	46.7	16.5		279752	334.1	9.9	20239	-63.0	-48.6	-39.0	-32.9	-36.8	-65.1
12.09.03	620	A12	4	0	0	0.0	0.0		48775	r	2.8							-54.9
12.09.03	620	A13	4	1	0	5.9	4.3		15338	r								-38.7
12.09.03	620	A14	4	0	0	1.1	0.1		7874	r								-25.5
12.09.03	620	B11	701233	1424	141	38.0	12.0		216	1517.0	180.7	40324	-69.6	-48.6	-39.6	-33.9	-38.2	-66.4
12.09.03	620	B12	8	0	1	0.0	0.0		46843	11.6	1.4	202311						-48.8
12.09.03	620	B13	8	0	0	0.0	0.0		15988	16.6	1.2	203900						-33.6
12.09.03	620	B14	94	1	1	0.0	0.0		8148	6.9	0.3	202966						-25.9
12.09.03	620	C11	51	0	1	0.1	0.0			9.1	5.1		-56.9					
12.09.03	620	C12	8	0	0	0.0	0.0			r	3.1	202270						
12.09.03	620	C13	5	0	1	0.0	0.1		1020	5.4	5.2	203069						-29.3
12.09.03	620	C14	342	21	5	1.0	0.4		1324	4.8	2.2							-23.2
18.09.03	626	A11	772804	1892	194	49.1	17.0		19976	577.3	9.8	21077	-65.1	-44.3	-39.2	-32.8	-36.8	-64.4
18.09.03	626	A12	38	0	0	0.0	0.0		45581	28.0								-56.4
18.09.03	626	A13							16245									-41.9
18.09.03	626	A14		9	0	0.0	0.0		9331	13.8								-24.9
18.09.03	626	B11	775216										-69.2	-53.2	-40.3	-33.6	-37.8	-68.7
18.09.03	626	B12	63	0	1	0.0	0.0		62724	25.1								-46.9
18.09.03	626	B13	8	0	0	0.0	0.0		18031	16.6	1.1							-34.9
18.09.03	626	B14							11055									-25.8

Appendix 3. Soil gas samples from the monitoring sites - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Well A3 (cont.)

Date	day	Location	C_1	C_2	C_3	iC_4	nC_4	C_{5+}	CO_2	He	H_2	O_2	δC_{C1}	δC_{C2}	δC_{C3}	δC_{iC4}	δC_{nC4}	δC_{CO2}
27.09.03	635	A14	5	0	0	0.0	0.0		9486	11.4		205436						-24.5
27.09.03	635	B11	834525	1895	190	47.8	17.0		255	989.4	235.7	16550	-69.1	-52.4	-40.3	-32.3	-36.7	-69.6
27.09.03	635	B12							65581				-55.8					-47.9
27.09.03	635	B13		8	0	0.7	0.1		20879			148945						-34.7
27.09.03	635	B14							10825									-25.4
27.09.03	635	C11	115	0	1	0.0	0.0		1552	8.2	0.8	202199						-46.2
27.09.03	635	C12	482	1	0	0.0	0.0		1442	7.0	0.7	197500						-41.5
27.09.03	635	C13	44	1	1	0.1	0.1		1208	5.4	0.8	203716						-29.5
27.09.03	635	C14							963									-17.6
02.10.03	640	A11	788300	1951	201	52.9	17.0		14951	588.3	8.4	20857	-65.4	-50.3	-39.7	-32.7	-37.8	-66.7
02.10.03	640	A12	1	0	0	0.0	0.0		47630	23.1	0.9	196533						-58.0
02.10.03	640	A13	1	0	0	0.0	0.0		12113	31.4	1.1	202173						-40.9
02.10.03	640	A14	2	0	0	0.0	0.0		6592	5.1	1.9	198039						-23.3
02.10.03	640	B11	815151	1834	182	47.1	15.2		167	960.4	186.6	10768	-69.3	-52.4	-40.7	-34.3	-39.1	-70.7
02.10.03	640	B12	1	0	0	0.0	0.0		49313	18.1	7.5	187041						-48.3
02.10.03	640	B13	1	0	0	1.6	3.5		13040	96.9	64.8	202920						-34.2
02.10.03	640	B14	3	0	0	0.2	0.1		8060	10.3	3.0	200287						-21.9
02.10.03	640	C11	2	0	0	0.0	0.0		2852	16.6	2.0	220342						-49.5
02.10.03	640	C12							939									-37.2
02.10.03	640	C13							697									-21.8
02.10.03	640	C14							1125									-18.7
16.10.03	654	A11	737971	1789	182	48.0	15.4		22456	548.5	7.4	13652	-64.7	-44.7	-39.4	-32.5	-37.0	-70.1
16.10.03	654	A12							24670									-59.1
16.10.03	654	A13	2	0	0	0.0	0.0		6020	39.7	1.1	206792						-42.5
16.10.03	654	A14	12	0	0	0.0	0.0		2717	45.3	0.5	212865						-23.5
16.10.03	654	B11	871930	1965	198	51.6	16.9		291	1105.0	167.9	18879	-68.6	-52.6	-40.3	-33.8	-38.0	-67.8
16.10.03	654	B12	1	0	0	0.0	0.0		23688	8.0	3.7	160869						-47.8
16.10.03	654	B13	16	0	0	0.0	0.0		7516	14.0	1.5	217958						-34.2
16.10.03	654	B14	23	0	0	0.2	0.3		3596	13.0	1.5	228112						-24.3
16.10.03	654	C11	2	0	0	0.0	0.0		1048	12.8	2.5	204954						-42.9
16.10.03	654	C12							960									-35.3
16.10.03	654	C13							718									-21.1
16.10.03	654	C14							753									-14.1
25.10.03	663	A11	822376	2003	204	54.1	17.5		21930	643.0	7.5	1707	-63.9	-44.0	-39.8	-33.4	-37.3	-68.4
25.10.03	663	A12							39849									-59.3
25.10.03	663	A13	1	0	0	0.0	0.0		8965	84.6	0.6	194752						-44.7
25.10.03	663	A14	1	0	0	0.0	0.0		4796	77.4	41.2	205436						-24.0
25.10.03	663	B11	849366	1914	190	49.2	15.9		333	1039.0	195.0	3374	-68.4	-46.2	-41.2	-33.6	-38.3	-65.2
25.10.03	663	B12	1	0	0	0.0	0.0		49335	44.6	4.5	183057						-46.5
25.10.03	663	B13	1	0	0	0.0	0.0		13192	347.6	265.0	211103						-33.3
25.10.03	663	B14	1	0	0	0.0	0.0		6573	88.9	0.9	211332						-24.2
25.10.03	663	C11	9	0	0	0.0	0.0		3914	71.7	0.0	199875						-53.3
25.10.03	663	C12	1	0	0	0.2	0.0		1121	98.4	0.3	199105						-38.2
25.10.03	663	C13							707									-22.4
25.10.03	663	C14							610									-13.5
08.11.03	677	A11	811344	1974	203	53.9	17.5		30045	645.0	7.3	2912	-64.5	-43.7	-39.8	-33.1	-36.5	-62.8
08.11.03	677	A12	3	0	0	0.0	0.0		32749	54.6	1.1	185374						-61.8
08.11.03	677	A13	1	0	0	0.0	0.0		7614	13.8	1.7	214145						-46.3
08.11.03	677	A14	1	0	0	0.0	0.0		3210	94.3	0.6	209735						-24.2
08.11.03	677	B11	821432	1852	184	47.9	15.7		218	1524.0	183.6	9006	-69.5	-46.0	-39.9	-33.1	-38.7	-62.6
08.11.03	677	B12	1	0	0	0.0	0.0		44484	243.7	3.2	168698						-47.3
08.11.03	677	B13							10706	250.0	113.8	187774						-34.7
08.11.03	677	B14	1	0	0	0.0	0.0		2411	108.4	0.6	203702						-24.6
26.11.03	695	A11	795949	1939	202	54.3	17.7		15058	592.9	4.8	1005	-63.8	-44.2	-39.1	-32.1	-35.9	-71.2
26.11.03	695	A12							23897									-63.9
26.11.03	695	A13	11	0	0	0.0	0.0		4992	18.7	0.4	195235						-48.3
26.11.03	695	A14	1	0	0	0.0	0.0		2241	250.8		187774						-23.4
26.11.03	695	B11	871930	1965		51.6	16.9		986	1105.0	370.2	18879	-69.3	-45.2	-40.2	-33.0	-37.4	-64.8
26.11.03	695	B12																
26.11.03	695	B13	1	0	0	0.0	0.0		8295	17.3	2.5	208936						-35.0
26.11.03	695	B14	1	0	0	0.0	0.0		3519	108.0	0.7	203702						-26.4
23.12.03	722	A11											-57.7	-41.9	-38.0	-31.7	-36.0	-73.9
23.12.03	723	A12							8075									-62.8
23.12.03	724	A13							4470									-48.5
23.12.03	725	A14							1730									-22.4
23.12.03	726	B11																
23.12.03	727	B12																
23.12.03	728	B13							6720									-34.3
23.12.03	729	B14							2423									-25.2

Appendix 3. Soil gas samples from the monitoring sites - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Well A3 (cont.)

Date	day	Location	C_1	C_2	C_3	C_4	C_5	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{C4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$
07.02.04	768	A11											-59.7	-41.9	-36.9	-31.0	-35.8	-76.8
07.02.04	768	A12							14074									-61.2
07.02.04	768	A13							4470									-42.7
07.02.04	768	A14							2307									-21.8
07.02.04	768	B11																
07.02.04	768	B12																
07.02.04	768	B13							8047									-39.0
07.02.04	768	B14							3778									-26.4
07.02.04	768	C11											-52.2					-55.3
16.04.04	867	A11	781469						2094				-66.7	-44.8	-38.8	-31.6	-35.6	-72.8
16.04.04	867	A12	13000						34873				-46.2					-62.4
16.04.04	867	A13							12789									-44.7
16.04.04	867	A14							6823									-28.1
16.04.04	867	B11											frozen					
16.04.04	867	B12	5054						24666				-47.9					-55.3
16.04.04	867	B13							14064									-41.2
16.04.04	867	B14																
16.04.04	867	C11							10729									-51.2
28.08.04	1002	A11	782420	1814	183	46.4	15.3		16506				-66.7	-44.2	-39.8	-32.9	-36.7	-56.3
28.08.04	1002	A12	13	3	1	0.3	0.4		33167									-47.1
28.08.04	1002	A13	10	0	2	0.1	0.2		21445									-26.8
28.08.04	1002	A14	19100	37	6	1.3	0.7		18315									-22.4
28.08.04	1002	B11	778777	1511	156	42.8	14.7		238				-69.7	-45.4	-39.2	-32.8	-36.9	-30.1
28.08.04	1002	B12																
28.08.04	1002	B13																
28.08.04	1002	B14																

Appendix 3. Soil gas samples from the monitoring sites - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Well A19

Date	day	Location	C_1	C_2	C_3	C_4	C_5	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$
29.09.99		110cm depth	386059	1226	129	21.8	11.0						-67.9	-43.7	-35.3	-30.9		-5.2
26.07.00		220cm depth	648334	1941	222	84.5	20.4	7.9	2068				-64.5	-42.6	-37.5	-33.9	-36.8	-40.5
13.07.01		5cm/70cm	113925	174	21	6.4	1.9	0.0	72424				-62.0	-45.5	-35.1	-29.3	-33.5	-82.1
23.08.01		5cm/70cm	635358	1552	151	34.6	12.7	15.9	45780				-66.9	-41.6	-35.0	-31.2	-34.6	-80.1
23.08.01		1.7m/70cm	134057	389	64	25.8	11.8	304.9	150814				-59.6	-41.9	-34.4	-31.4	-31.4	-31.6
23.08.01		5m/70cm	34	0	0	0.0	0.0	4.4	669									-17.2
23.08.01		5m offlease	8	0	0	0.0	0.1	17.2	2152									-24.6
02.11.01		50cm/70cm	953338	3762	349	####	67.0	22.1	2821				-60.9	-41.8	-35.0	-30.7	-33.2	-67.4
02.11.01		1m/70cm	832759	2785	32	30.7	1.5	81.3	83050				-59.0	-38.9	-32.6	-29.1		-47.3
02.11.01		2m/70cm	61546	187	8	3.5	1.1	96.2	12634				-54.0	-36.9	-31.4			-34.6
02.11.01		3m/70cm	564323	1896	66	27.0	6.3	488.3	81323				-55.2	-37.2	-27.8	-26.5		-34.9
02.11.01		4m/70cm	561334	1816	42	21.2	2.8	266.0	36534				-56.4	-38.3	-26.7			-39.1
02.11.01		5m/70cm	643783	?	?	?	?	20.9	36807				-55.3	-38.4				-40.8
02.11.01		5 out off lease	108	1	0	0.1	0.0		7199				-50.1					-35.9
25.06.02		GB1											-68.5	-44.0	-36.2			-24.3
25.06.02		GB2											-63.2	-40.9				-24.7
25.06.02		GA1											-61.6	-41.7	-35.6	-30.8	-36.0	-35.7
25.06.02		GA2											-52.0	-36.6	-34.2			-32.8
25.06.02		GA3											-57.2	-41.2				-28.2
25.06.02		GA4											-58.8	-42.1	-32.0	-29.1	-32.4	-27.4
25.06.02		GA5											-52.0	-35.1	-30.8			-28.2
25.06.02		GA6											-47.0					-32.5
27.06.02		GB1											-70.0	-45.3	-36.2			-22.1
27.06.02		GB2											-60.6	-43.0	-34.1			-26.7
27.06.02		GA1											-62.8	-41.9	-35.1			-29.4
27.06.02		GA2											-56.3	-38.6	-32.9	-29.8		-31.2
27.06.02		GA3											-55.8	-38.5	-31.3			-25.4
27.06.02		GA4											-49.4	-37.6	-32.9			-31.7
27.06.02		GA5											-42.2	-31.9	-27.9			-27.6
27.06.02		GA6											-44.7	-31.5				-32.3
27.06.02		GC1											-63.6	-40.2	-34.4	-31.0	-34.8	-75.4
27.06.02		GC2											-41.6					-45.8
27.06.02		GC3																-19.8
27.06.02		GC4																-18.8
27.06.02		GC5																-20.8
27.06.02		GC6																-16.7
11.07.02	191	GB1											-63.4	-41.1	-35.5	-26.9	-30.2	-22.4
11.07.02	191	GA1	738257	2808	262	51.3	24.9		10561	1178.7	11.2	14488	-65.7	-40.0	-35.4	-33.6	-31.5	-36.0
11.07.02	191	GA2	120655	452	55	17.2	15.5		70113	227.4	6.2	9873	-62.6	-39.4	-33.3	-30.5	-29.2	-37.0
11.07.02	191	GA3	96389	460	51	21.4	46.0		114989	91.7	28.0	12074	-48.3	-33.7	-30.3			-32.4
11.07.02	191	GA4	88802	482	32	14.9	21.2		151828	56.0	32.6	12339	-46.0	-33.6	-30.4			-30.5
11.07.02	191	GA5	27460	156	15	<0.01	8.1		191742	30.5	4.2	16230	-41.6	-30.9	-28.0			-30.4
11.07.02	191	GA6	1119	5	0	<0.01	0.2		60597	8.8	1.0	41622	-41.4					-33.9
11.07.02	191	GC1	246289	743	73	16.8	6.5		19365	332.8	4.0		-68.1	-38.6	-37.2	-33.8		-74.0
11.07.02	191	GC2	13	0	0	0.0	0.1		2206	17.1								-53.5
11.07.02	192	GC3	15	0	0	0.0	0.1		1679	nd								-24.5
11.07.02	193	GC4	5	<0.01	<0.01	<0.01	0.0		1136	nd	0.8							-26.4
11.07.02	194	GC5	4	<0.01	<0.01	<0.01	0.0		888	nd								-23.1
11.07.02	195	GC6	4	<0.01	<0.01	<0.01	0.0		2681	nd								-26.9
21.07.02	202	GA1																
21.07.02	202	GA2	103063	392	46	14.7	12.8		57358	169.1	5.3		-60.7	-38.6	-32.4	-29.3	-28.9	-40.3
21.07.02	202	GA3	115317	497	51	21.6	53.1		73953	141.6	758.6	5311	-51.4	-35.6	-32.5	-29.7		-33.7
21.07.02	202	GA4	123085	603	51	21.5	33.4		114824	108.8	33.1	14745	-48.6	-35.9	-30.7			-29.9
21.07.02	202	GA5	41562	146	12	7.6	9.0			69.0	12.3	15701	-55.0	-35.0				-30.3
21.07.02	202	GA6	1150	4	0	0.2				12.3	1382.9	1574	-52.1					-32.5
21.07.02	202	GA7	5							nd								
21.07.02	202	GC1	534189	1094	79	25.1	4.2		3244	769.8	2.7		-63.8	-39.2	-33.0	-30.4		-73.1
21.07.02	202	GC2	592	2	0	0.0			1619	19.1			-56.8					-50.3
21.07.02	202	GC3	84	0	0	0.0	0.1		362	nd								-17.8
21.07.02	203	GC4	38	0	0	0.0			196	nd								-19.4
21.07.02	204	GC5	23	0	0				661	nd								-21.5
21.07.02	205	GC6	23	0	0	0.0			354	nd								-21.7

Appendix 3. Soil gas samples from the monitoring sites - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Well A10 (cont.)

Date	day	Location	C_1	C_2	C_3	C_4	C_5	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$
08.09.02	251	GA1	926400	2875	325	60.9	33.0		249	1133.3	30.8	17778	-65.6	-41.5	-35.4	-31.2	-35.9	-96.1
08.09.02	251	GA2	143911						77888			17817	-61.1	-38.7	-31.9	-28.7	-34.1	-50.7
08.09.02	251	GA3	164600	467	65	19.6	18.4			195.3	12.7		-52.4	-35.9	-31.0	-28.0	-29.9	-33.1
08.09.02	251	GA4	78620	205	21	8.8	13.1		28088	67.7	11.3		-56.7	-34.3	-32.2	-28.0	-26.3	-31.5
08.09.02	251	GA5	186500	329	12	6.5	7.4		132886	130.0	21.2		-57.0	-38.6	-28.6	-26.0	-27.1	-31.4
08.09.02	251	GA6	41189	69	3	0.4	0.3		188812	41.6	8.4	17023	-54.6	-39.8	-30.5	-30.6	-23.4	-32.1
08.09.02	251	GA7	41	2	1	0.6	0.2		1681	7.5	1.2	163143	-61.2					-30.9
08.09.02	251	GC1	181400	302	31	9.0	2.2		6293	218.4	1.2		-60.3	-36.6	-31.1			-69.6
08.09.02	251	GC2	1455	2	0	0.1	0.1		3121	n.a	1.4		-61.0					-56.5
08.09.02	251	GC3	55	0	0	0.0	0.1		759	15.4	4.8		-62.8					-26.2
08.09.02	251	GC4																
08.09.02	252	GC5	102	0	1	0.1	0.1		377	6.1		200050	-49.0					-20.5
08.09.02	253	GC6	19	0	0	0.0	0.0			8.0	5.8		-46.1					-22.4
31.10.02	304	GA1	690326	2598	244	47.5	23.2		61	1121.4	6.9	7881	-65.4	-40.1	-35.2	-29.4	-33.6	-66.5
31.10.02	304	GA2																
31.10.02	304	GA3	143161	531	47	15.8	33.8			160.8	2.0	43343	-55.2	-36.5	-31.4	-27.8	-25.9	-37.1
31.10.02	304	GA4	129612	424	9	4.3	4.1		48023	92.7	8.3		-56.6	-34.8	-30.9	-27.5	-28.3	-31.3
31.10.02	304	GA5	129612	424	9	4.3	4.1			92.7	8.3	26249	-48.8	-37.1	-27.6	-26.4		-33.1
31.10.02	304	GA6	12079	47	1	0.3	0.1		94917	35.9	2.7	21444	-44.3					-35.2
31.10.02	304	GA7	3				0.0			5.7	1.6							-33.3
31.10.02	304	GC1	375402	1498	142	29.7	13.4		169	414.5	1.6		-61.2	-39.6	-34.2	-26.9		-59.6
31.10.02	304	GC2	72872	255	22	4.5	1.9		763	85.7	1.8		-63.3	-40.8	-37.3			-54.6
31.10.02	304	GC3	1283	2	0	0.1	0.5		291	16.7			-62.8					-28.2
31.10.02	304	GC4	83	0	0				764				-64.9					-21.4
31.10.02	305	GC5	46	0	0	0.0	0.0		1067		1.8		-52.8					-20.1
31.10.02	306	GC6	25	0	0	0.0	0.0		963	16.9	1.4		-44.5					-14.7
21.11.02	328	GA1	944604	3089	320	58.0	29.7		225	1190.9	8.3	14657	-65.3	-41.4	-35.6	-31.3	-35.2	-47.4
21.11.02	328	GA2																
21.11.02	328	GA3	374838	1007	101	32.0	74.8		32192	321.9	2.6	12380	-57.3	-37.4	-31.7	-29.5	-28.2	-40.3
21.11.02	328	GA4																
21.11.02	328	GA5	112848	390	9	5.0	4.6		93752	73.4	3.8	26887	-46.0	-34.2	-28.4	-36.1	-35.2	-31.2
21.11.02	328	GA6																
21.11.02	328	GA7	11	0	0	0.0	0.0		1261	7.6	2.2		-53.3					-32.9
21.11.02	328	GC1																
21.11.02	329	GC2																
21.11.02	330	GC3																
21.11.02	331	GC4																
21.11.02	332	GC5																
21.11.02	333	GC6																
17.12.02	351	GA1	961289	3072	316	56.8	28.6		100	1232.5	6.9	17338	-66.0	-41.8	-35.5	-32.1	-34.2	-42.2
17.12.02	351	GA2																
17.12.02	351	GA3	493660	1319	115	38.4	67.4		22120	395.7	1.7	8753	-56.9	-38.0	-31.5	-29.7	-27.0	-37.9
17.12.02	351	GA4																
17.12.02	351	GA5	87773	246	8	4.9	4.6		73345	66.7	3.2	28950	-49.5	-31.8	-27.0			-31.0
17.12.02	351	GA6	5526	10	0	0.1	0.1		110060	32.7		20087	-49.3					-37.4
17.12.02	351	GA7	9	0	0	0.0	0.0		35128	17.0								-33.6
24.01.03	389	GA1	701805	2194	225	40.6	20.6		346	844.2	5.5	80520	-65.3	-42.6	-38.2	-34.4	-33.7	-26.7
24.01.03	389	GA2																
24.01.03	389	GA3	394128	1166	80	29.3	58.9		24633	306.9	3.8	19656	-59.2	-39.9	-31.0	-27.3	-24.8	-36.8
24.01.03	389	GA4																
24.01.03	389	GA5	79064	248	7	4.9	4.2		60703	59.8	1.9	20839	-51.0	-35.3	-25.8	-26.0	-26.3	-33.3
24.01.03	389	GA6	13664	36	1	0.1	<0.01		69310	28.3		57383	-52.7	-30.3				-37.5
24.01.03	389	GA7																
04.03.03	425	GA1	885142	2769	284	50.9	25.7			1098.7	6.2	20631	-66.0					
04.03.03	425	GA2																
04.03.03	425	GA3	231664	681	44	14.8	25.2		27260	193.1	371.9	15673	-60.3	-38.2	-30.4			-37.7
04.03.03	425	GA4																
04.03.03	425	GA5	63882	188	5	2.5	<0.01			43.5	5532.3	53989	-53.3			-26.3	-25.9	-31.9
04.03.03	425	GA6	22185	64	2	0.5	0.2			27.9	2.7			-35.5				
04.03.03	425	GA7																
27.03.02	451	GB1	735274	2270	203	48.0	<0.01		1105	856.9	350.2	59538	-65.9	-44.3	-34.6	-26.7	-27.[illegible]	-62.9
27.03.03	451	GA1	821192	2486	216	40.0	<0.01			981.2	48.2							
27.03.03	451	GA2																
27.03.03	451	GA3	181992	543	37	14.0	29.0			162.0	1703.0	5454						
27.03.03	451	GA4																
27.03.03	451	GA5	45819	137	4	3.0	2.0			33.0	865.0	42767						
27.03.03	451	GA6	16687	371	4	1.3	0.3			161.8		73613	-70.9					
27.03.03	451	GA7	2554	2	0	0.0	0.0			25.8								

Appendix 3. Soil gas samples from the monitoring sites - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Well A 10 (cont.)

Date	day	Location	C_1	C_2	C_3	C_4	C_5	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{iC4}$	$\delta^{13}C_{nC4}$	$\delta^{13}C_{CO2}$
01.05.02	486	GB1	768922	2393	219	45.1	<0.01		806	915.0	121.3	35105	-64.3	-41.7	-35.3	-27.0	-28.0	-32.4
01.05.03	486	GA1																
01.05.03	486	GA2																
01.05.03	486	GA3	311359	700	40	30.5	<0.01		35381	431.4	4018.5	415410	-64.2	-39.8	-32.9	-27.9	-25.0	-35.2
01.05.03	486	GA4																
01.05.03	486	GA5																
01.05.03	486	GA6																
01.05.03	486	GA7	405688	989	59	12.1	6.7		989	205.3				-33.6	-30.5	-26.8	-26.3	-31.3
19.06.03	534	GB1	912065	3008	312	57.3	29.2		31	1103.9	4.0	3950	-64.6					
19.06.03	535	GA1																
19.06.03	535	GA2	338006	799	53	46.1	nd			422.6	2.0	34264						
19.06.03	535	GA3	483047	865	41	31.2	nd			590.5	3.9							
19.06.03	535	GA4	455126	1725	80	8.3	nd			184.9	217.4	34264						
19.06.03	535	GA5																
19.06.03	535	GA6	35	0	0	nd	0.0			23.5	2.3							
19.06.03	535	GA7	361351	1816	96	22.0	7.5			349.0	1.4	37013	-61.0					-72.6
19.06.03	535	GC1																
19.06.03	535	GC2	6557	25	3	0.6	0.3			14.6								
19.06.03	535	GC3	37	0	0	0.1	nd			nd								
19.06.03	535	GC4	32	0	0	0.1	0.1			nd								
19.06.03	535	GC5	22	0	0	0.0	0.0											
19.06.03	536	GC6	14	0	0	0.0												
09.08.03	582	GA1	436970	1469	155	29.6	15.2		67	1114.8	22.3	18147	-64.3	-40.6	-35.3	-31.3	-36.8	-61.3
09.08.03	582	GA2	193800	519	25	12.2	15.5		1038	175.2			-64.6	-42.0	-35.8	-29.0	-37.9	-66.0
09.08.03	582	GA3	153300	603	30	11.5	5.8		15501		18.6	66004	-57.6	-38.9	-31.5	-25.9	-31.3	-34.5
09.08.03	582	GA4	78617	205	21	9.0	13.0			4.8	1.0	201200	-48.1					-30.6
09.08.03	582	GA5	24150	123	6	2.0	0.9				0.4	187186						
09.08.03	582	GA6	4							6.4	4.2	293900	-49.0					-32.8
09.08.03	582	GA7																-32.8
09.08.03	582	GC1	146048	460	42	8.9	5.8		2937	304.0	5.5	371412	-63.6					-68.7
09.08.03	582	GC2	7742	28	3	0.7	0.3		4869	44.7	4.7	178200	-68.7					-64.7
09.08.03	582	GC3	437	2	0	0.1	0.1			7.0	3.7	190800						
09.08.03	582	GC4	95	1	0	0.0	0.1			7.3	0.6	197300						
09.08.03	583	GC5	10	0	0	0.0	0.0			4.9	1.3	199400						
09.08.03	584	GC6									0.3							
28.08.03	605	GA1	949177	2975	338	64.4	35.7		218	1181.8	21.4	12896	-64.2	-41.4	-34.6	-28.5	-35.6	-63.4
28.08.03	605	GA2																
28.08.03	603	GA3	496200	1218	93	34.3	67.4			342.7	3.3	15354						
28.08.03	605	GA4	442100	1140	66	31.1	43.3			195.2	5.4	18423						
28.08.03	605	GA5	244500	963	53	19.0	10.5			109.0	2.0	15354						
28.08.03	605	GA6	24310	89	6	2.2	1.1			38.1	3.0	75007						
28.08.03	605	GA7	1009	2	1	0.1	0.0			7.0	1.8							
28.08.03	605	GC1	482500	1515	146	33.7	12.5		5425	387.6	5.1	287496	-59.7					-69.9
28.08.03	605	GC2	5534	9	2	0.3	0.1			31.9	1.9	199236						
28.08.03	603	GC3	542	1	1	0.1	0.0			19.9	4.9	199389						
28.08.03	605	GC4	48	0	1	0.0	0.0			4.5	0.8	205464						
28.08.03	606	GC5	1517	2	1	0.1	0.1			3.5	0.4	204500						
28.08.03	607	GC6	30	0	1	0.0	0.0			4.5	0.2	202500						
12.09.03	620	GA1	926440	2875	325	60.9	33.0			1133.0	31.0	17547						
12.09.03	620	GA2																
12.09.03	620	GA3	786166	205	21	8.8	13.0			67.7	12.7	31108						
12.09.03	620	GA4	186500	327	12	6.5	4.4			130.0	11.3							
12.09.03	620	GA5	14890	69	3	0.4	0.3			41.4	21.0	82333						
12.09.03	620	GA6										108523						
12.09.03	620	GA7	17	2	1	0.6	0.2			6.4	11.5							
12.09.03	621	GC1	164600	476	65	19.6	18.4			195.3	9.4							
12.09.03	622	GC2	181400	302	31	9.0	2.2			218.4	12.7							
12.09.03	623	GC3	1455	2	0	0.1	0.1			r	1.2							
12.09.03	624	GC4	55	0	0	0.0	0.1			15.4	5.0							
12.09.03	625	GC5	102	0	1	0.1	0.1			6.1								
12.09.03	626	GC6	19	0	0	0.0	0.0			8.0	6.3							
16.10.03	654	GA1	612412	1770	183	30.6	16.2			1081.3	6.5	21397	-65.2	-42.2	-35.3	-31.2	-36.2	-64.9
16.10.03	654	GA2																
16.10.03	654	GA3											-58.8	-39.2	-32.2	-28.4	-25.0	-36.6
16.10.03	654	GA4											-51.5	-36.5	-31.1	-28.4	-25.9	-30.3
16.10.03	654	GA5											-52.6	-34.9	-27.8	-27.3	-26.8	-31.2
16.10.03	654	GA6											-51.1	-35.7	-25.3			-33.1
16.10.03	654	GA7							94644									-32.5
16.10.03	654	GC1											-65.4	-40.5	-34.0	-29.9	-33.1	-73.9
16.10.03	654	GC2							1050				-64.9					-14.1
16.10.03	654	GC3							1231				-58.7					-20.2
16.10.03	654	GC4							744				-57.2					-13.6
16.10.03	655	GC5							919				-40.4					-12.6
16.10.03	656	GC6							1406				-33.5					-17.3

Appendix 3. Soil gas samples from the monitoring sites - concentrations (ppmv) and $\delta^{13}C$ (‰, VPDB)

Well A10 (cont.)

Date	. day	Location	C_1	C_2	C_3	C_4	C_5	C_{6+}	CO_2	He	H_2	O_2	$\delta^{13}C_{C1}$	$\delta^{13}C_{C2}$	$\delta^{13}C_{C3}$	$\delta^{13}C_{C4}$	$\delta^{13}C_{C5}$	$\delta^{13}C_{CO2}$
25.10.03	663	GA1											-63.8	-41.8	33.2	-31.7	-36.7	-24.3
25.10.03	663	GA2																
25.10.03	663	GA3											-56.4	-39.1	-32.3	-28.5	-25.6	-37.2
25.10.03	663	GA4											-51.8	-36.1	-30.8	-28.6	-25.3	-31.0
25.10.03	663	GA5											-50.1	-35.6	-28.0	-27.2	-25.4	-31.2
25.10.03	663	GA6											-52.2	-31.9				-33.9
25.10.03	663	GA7							78447									-32.4
25.10.03	663	GC1											-63.1	-31.1				-21.7
25.10.03	663	GC2											-58.5					-66.1
25.10.03	663	GC3							1211									-16.0
25.10.03	663	GC4							1269									-15.7
25.10.03	664	GC5							1516									-18.9
25.10.03	665	GC6							1647									-20.2
08.11.03	677	GA1											-65.9	-42.0	-35.3	-31.1	-33.9	-62.[illegible]
08.11.03	677	GA2																
08.11.03	677	GA3											-58.9	-40.1	-32.6	-25.7	-25.6	-41.8
08.11.03	677	GA4											-54.2	-36.7	-30.6	-27.2	-25.1	-31.5
08.11.03	677	GA5											-48.3	-35.2	-27.9	-27.7	-25.7	-31.5
08.11.03	678	GA6											-48.9	-35.8				-35.0
08.11.03	679	GA7							52975									-33.3
23.12.03	726	GA1											-62.7	-41.8	-34.9	-30.6	-35.6	-60.0
23.12.03	727	GA2																
23.12.03	728	GA3											-57.1	-38.7	-32.3	-29.0	-26.5	-34.6
23.12.03	728	GA4											-51.3	-38.1	-31.8	-28.2	-25.8	-30.9
23.12.03	728	GA5											-48.3	-35.2	-28.5	-27.2	-26.8	-32.2
23.12.03	728	GA6											-49.8					-34.7
23.12.03	728	GA7							99270									-32.9
07.01.04	768	GA1																
07.01.04	768	GA2																
07.01.04	768	GA3											-59.8	-39.6	-32.9	-30.5	-25.9	-36.0
07.01.04	768	GA4											-56.5	-37.8	-30.5	-28.1	-26.4	-31.5
07.01.04	768	GA5											-52.2	-35.9	-28.5	-25.7	-24.0	-32.1
07.01.04	768	GA6											-61.4	-34.3				-33.5
07.01.04	768	GA7							153433									-33.1

Appendix 4. Carbon stable isotope composition, amount, fraction of authigenic calcite, and pH of soil samples.

Date	Sample location (UWI)	Distance from well (cm)	Depth (cm)	Sample type	$\delta^{13}C_{calcite}$ (‰, VPDB)	$\delta^{18}O_{calcite}$ (‰, VPDB)	$\delta^{18}O_{calcite}$ (‰, VSMOW)	Total calcite (mg/kg)	Authigenic carbonate (%)	Authigenic carbonate (mg/kg)	$\delta^{13}C_{SOM}$ (‰, VPDB)	SOM amount (%)	pH
25.11.2001	EDAM A3-17-048-19W3	30	20	bulk	-30.5	-15.5	15.0	15	58	9	-31.5		7.8
"	"	30	50	bulk	-57.2	-18.7	11.8	122	100	122	-43.9	0.5	8.3
"	"	30	50	selected	-55.1	-20.0	10.4						
Jul-04		30	50										
"	"	30	70	bulk	-48.8	-17.4	13.0	23	80	19	-35.6	0.2	8.6
"	"	30	70	selected	-55.9	-17.2	13.2						
"	"	30	100	bulk	-44.6	-15.9	14.6	109	74	80	-34.7	0.5	7.3
"	"	30	150	bulk	-42.1	-13.6	16.9	1222	68	831	-30.6	0.2	10.9
"	"	30	150	selected	-57.6	-16.9	13.5						
Jul-04	"	30	150										8.2
Jul-04	"	30	185										9.0
		30	200	bulk	-32.3	-17.0	13.4	45	48	21	-29.0	0.2	8.7
"	"	200	20	bulk	-36.9	-16.9	13.6	36	75	27	-38.2	0.4	5.7
"	"	200	100	bulk	-45.9	-13.6	16.9	12	84	10	-35.1	0.4	7.1
"	"	200	200	bulk	-26.4	-12.3	18.3	197	40	80		0.3	8.6
"	"	200	200	selected	-31.7	-16.9	13.5						
"	"	400	20	bulk	-8.8	-7.1	23.4	89	0	0	-27.3	0.2	7.1
"	"	400	100	bulk	-11.1	-17.9	12.6	108	0	0	-27.6	0.23	7.5
"	"	400	210	bulk	-5.9	-14.1	16.4	10	0	0	-28.2	0.08	8.0
"	"	550	50	bulk	-8.9	-13.6	16.9	57	0	0	-28.7	0.21	7.6
"	"	550	100	bulk	-12.7	-19.2	11.3	115	0	0	-29.3		8.2
"	"	550	150	bulk	-14.5	-16.3	14.1	96	0	0	-28.9	0.19	8.0
"	"	550	200	bulk	-11.0	-13.6	16.9	7	0	0	-31.4	0.17	7.7
"	"	550	220	bulk							-28.9	0.15	8.5
"	"	550	250	bulk	-4.0	-11.5	19.0	4495					8.8
		550	270										8.4
"	"	550	300	bulk	-5.6	-9.4	21.1	33017					8.5
"	"	550	400	bulk	-2.7	-8.6	21.9	46095					
"	"	550	450	bulk	-3.1	-9.4	21.2	38793					
"	"	550	500	bulk	-4.0	-9.6	20.9	45276					
"	"	550	600	bulk	-5.4	-11.8	18.7	24250					

Appendix 4. Carbon stable isotope composition, amount, fraction of authigenic calcite, and pH of soil samples.
(cont.)

Date	Sample location (UWI)	Distance from well (cm)	Depth (cm)	Sample type	$\delta^{13}C_{calcite}$ (‰,VPDB)	$\delta^{18}O_{calcite}$ (‰,VPDB)	$\delta^{18}O_{calcite}$ (‰,VSMOW)	Total calcite (mg/kg)	Authigenic carbonate (%)	Authigenic carbonate (mg/kg)	$\delta^{13}C_{SOM}$ (‰,VPDB)	SOM amount (%)	pH
	EDAM												
18.06.2002	A4-17-048-19W3	20	20	bulk	-35.0	-22.1	8.4	32	64	20	-48.8	n.d.	7.5
"	"	20	50	bulk	-53.2	-20.6	9.9	488	91	444	-36.0	0.26	8.4
18.06.2002	A4-17-048-19W3	20	70	bulk	-42.5	-19.8	10.5	86	89	77	-30.0	0.22	8.8
"	"	20	100	bulk	-15.2	-13.3	17.2				-30.3	n.d.	7.93
"	"	20	150	bulk	-15.8	-13.7	16.8	41582	25	10396			9.5
"	"	100	20	bulk	-9.6	-12.6	17.9	81	0	0	-27.2	n.d.	7.9
"	"	100	50	bulk	-19.6	-18.5	11.9	13	27	3	-28.8	0.21	7.4
"	"	100	100	bulk	-10.4	-17.2	13.2	41	0	0	-28.6	0.15	8.0
"	"	100	150	bulk	-18.0	-10.0	20.6	246	22	54	-30.9	0.28	8.2
"	"	100	200	bulk	-6.0	-10.4	20.2	50	0	0	-30.8	0.20	8.1
"	"	200	20	bulk	-15.5	-15.5	15.0				-26.4	0.64	7.5
"	"	200	50	bulk	-18.7	-9.1	21.6	110	45	49	-28.5	0.15	8.1
"	"	200	100	bulk	-15.8	-10.4	20.2	220	1	2	-32.1	0.16	7.9
		200	150	bulk							-28.1	0.44	
"	"	400	20	bulk	-14.4	-14.3	16.2	181			-29.1	0.20	7.5
"	"	400	50	bulk	-16.7	-19.1	11.2	222				0.20	7.8
"	"	400	100	bulk	-17.3	-19.5	10.9	212			-30.9	0.17	7.8
"	"	400	150	bulk	-16.7	-18.2	12.2	229			-29.6	0.20	7.6
"	"	400	200	bulk	-18.7	-18.1	12.2	146			-30.2	0.17	7.6
"	Background	10000	50	bulk	-9.8	-8.5	22.1	25			-29.1	0.22	8.3
"	"	10000	150	bulk	-13.9	-10.6	20.0	114			-29.9	0.21	7.5
"	"	10000	200	bulk	-0.3	-5.9	24.9	15			-31.1	0.16	7.7
24.08.2001	A10-36-48-23W3	20	100	bulk	-3.3	-11.1	19.5	6256					9.1
22.08.2001	14C-28-048-19W3	20	100	bulk	-5.4	-13.0	17.5	15490					8.1
"	"	100	100	bulk	-6.4	-10.4	20.1	8622					8.2

Appendix 4. Carbon stable isotope composition, amount, fraction of authigenic calcite, and pH of soil samples. (cont.)

Date	Sample location (UWI)	Distance from well (cm)	Depth (cm)	Sample type	$\delta^{13}C_{calcite}$ (‰,VPDB)	$\delta^{18}O_{calcite}$ (‰,VPDB)	$\delta^{18}O_{calcite}$ (‰,VSMOW)	Total calcite (mg/kg)	Authigenic carbonate (%)	Authigenic carbonate (mg/kg)	$\delta^{13}C_{SOM}$ (‰,VPDB)	SOM amount (%)	pH
	MAIDSTONE												
25.06.2002	A10-11-048-23W3	**50**	20	bulk	-21.3	-16.7	13.8	921					8.1
"	"	50	20	selected	-16.5	-10.0	20.6						
"	"	50	50	bulk	-9.3	-10.3	20.3	12315					7.9
		50	70										8.3
"	"	50	100	bulk	-9.7	-14.2	16.3	18670					8.4
"	"	50	165	bulk	-3.3	-11.5	19.0	35776					9.2
		100	50	bulk	-11.9	-15.7	14.7	6675					7.4
"	"	100	100	bulk	-8.0	-16.4	14.0						8.4
"	"	**200**	20	bulk	-4.5	-11.6	18.9						8.7
"	"	200	50	bulk	-1.1	-9.5	21.1	7362					7.0
"	"	200	100	bulk	-7.2	-16.4	14.0	11502					9.1
		400	20	pendant	-5.5	-14.2	16.3						
"	"	400	20	bulk	-4.9	-12.0	18.5	9296					8.8
"	"	400	50	bulk	-9.9	-16.7	13.7	2966					7.6
"	"	400	100	bulk	-5.5	-14.2	16.3						9.3
"	"	**600**	20	bulk	-4.6	-11.9	18.6	9138					8.7
"	"	600	50	bulk	-7.5	-14.8	15.7	16453					7.9
"	"	600	100	bulk	-7.0	-10.6	19.9						
"	"	**800**	20	bulk	-6.2	-12.3	18.3	7635					8.7
			50										7.6
"	"	800	100	bulk	-5.7	-15.2	15.2	12845					8.2
"	"	**1200**	20	bulk	-1.1	-9.5	21.2						
"	"	1200	50	bulk	-7.7	-14.2	16.3	6305					8.4
"	"	1200	100	bulk	-6.5	-11.0	19.6	13793					8.5
"	"	**1900**	50	bulk	-12.0	-13.6	16.7						8.0
"	"	**2200**	50	bulk	-11.4	-5.3	25.2	1672					8.5
"	"	2200	100	bulk	-3.3	-11.2	19.3	42155					8.8

Appendix 4. Carbon stable isotope composition, amount, fraction of authigenic calcite, and pH of soil samples. (cont.)

Date	Sample location (UWI)	Distance from well (cm)	Depth (cm)	Sample type	$\delta^{13}C_{calcite}$ (‰, VPDB)	$\delta^{18}O_{calcite}$ (‰, VPDB)	$\delta^{18}O_{calcite}$ (‰, VSMOW)	Total calcite (mg/kg)	Authigenic carbonate (%)	Authigenic carbonate (mg/kg)	$\delta^{13}C_{SOM}$ (‰, VPDB)	SOM amount (%)	pH
"	"	2200	150	bulk	-2.6	-9.9	20.6	16552					8.7
"	"	2200	200	bulk	-3.1	-9.8	20.7	39138					8.6
"	"	2200	350	bulk	-2.3	-9.0	21.5	45000					
08.09.2001	A6-21-48-23W3	20	100	bulk	-7.8	-10.2	20.3	7888			soil gas		9.7
08.09.2001	2D8-11-48-23W3	20	100	bulk	-8.9	-13.3	17.2	45707					9.3
13.07.2001	B4-12-48-23W3	20	100	bulk	-11.2	-8.8	21.7	13793	20	2759			9.5
		500	70					7305					7.7
	MAIDSTONE												
28.08.2001	2C10-11-48-23W3	20	100	bulk	-9.3	-9.5	21.2	14138					8.2
"	"	500	100	bulk	-3.3	-10.4	20.1	27241					8
"	"	3000	100	bulk	-2.4	-9.4	21.2	15183					8.5
02.11.2001	2D13-11-048-23W3	20	100	bulk	-15.2	-3.6	27.2						
		ABERFELDY											
08.09.2003	A7-02-049-27W3	20	100	CH4 zone	bulk	-6.6	-11.5	19	15090				
08.09.2003	C4-16-049-26W3	casing	**C4-16-Rust**	crust	-26.6	-15.1	15.3						
"	"	"	C4-16	crust	-29.3	-13.2	17.0						
"	"	"	C4-16 AWTS	selected	-32.9	-12.6	17.9						
			C4-16 AWTS	selected									8.5
													7.6
													7.5
08.09.2003	A9-17-049-26W3	casing	**A9-17 AWT**	crust	-12.8	-16.4	14.0						
"	"	"	100	crust	-12.3	-15.5	14.9						
"	"	5	210	bulk	-5.3	-10.7	19.8	25862					8.5
"	"	5	246	bulk	-17.4	-11.4	19.2	49310					8.8

Appendix 4. Carbon stable isotope composition, amount, fraction of authigenic calcite, and pH of soil samples. (cont.)

Date	Sample location (UWI)	Distance from well (cm)	Depth (cm)	Sample type	$\delta^{13}C_{calcite}$ (‰,VPDB)	$\delta^{18}O_{calcite}$ (‰,VPDB)	$\delta^{18}O_{calcite}$ (‰,VSMOW)	Total calcite (mg/kg)	Authigenic carbonate (%)	Authigenic carbonate (mg/kg)	$\delta^{13}C_{SOM}$ (‰,VPDB)	SOM amount (%)	pH
08.09.2003	A5-16-049-26W3	casing	**A5-16 AWT**	crust	-16.6	-15.4	15.1						8.3
"	"	"	A5-16 BWT	crust	-45.6	-17.1	13.3						8.4
"	"	"	A5-16 BWT s	selected	-46.2	-16.8	13.6						
"	"	"	145 cm	bulk									8.0
"	"	"	195 cm	bulk									8.0
"	"	"	250 cm	bulk									8.3
"	"	"	287 cm BBA(	bulk									8.8
08.09.2003	C8-17-049-26W3	casing	**C8-17 AWT**	crust	-27.4	-15.4	15.0						
"	"	"	C8-17 BWT	crust	-24.7	-14.7	15.8						
"	"	"	C8-17ABS	crust	-36.8	-13.1	17.4						
"	"	"	C8-17 BBAG	crust	-31.1	-15.2	15.3						
"	"	"	C8-17 BBAG	selected	-32.1	-14.2	16.3						
"	"	"	C8-17 lowest	selected	-32.7	-13.7	16.8						
"	"	"	135	bulk									7.6
"	"	"	177	bulk									8.5
	ABERFELDY												
08.09.2003	C8-17-049-26W3												
"	"	"	210	bulk									8.8
"	"	"	233	bulk									8.4
			264	bulk									8.5
08.09.2003	13-19-049-26W3	casing	**13-19S**										
"	"	"	182	bulk									8.3
"	"	"	210	crust	-44.1	-17.3	13.1						9.3
				selected	-48.3	-16.1	14.2						
"	"	"	270	bulk									9.0
"	"	"	310	bulk									9.1
08.09.2003	C6-16-049-26W3	casing		crust	-38.2	-12.7	17.8						7.1
													7.8